EPTEMBER, 1943 ONE SHILLING

Plastics

DEALING WITH THE MANUFACTURE, USES AND POTENTIALITIES OF PLASTIC MATERIALS

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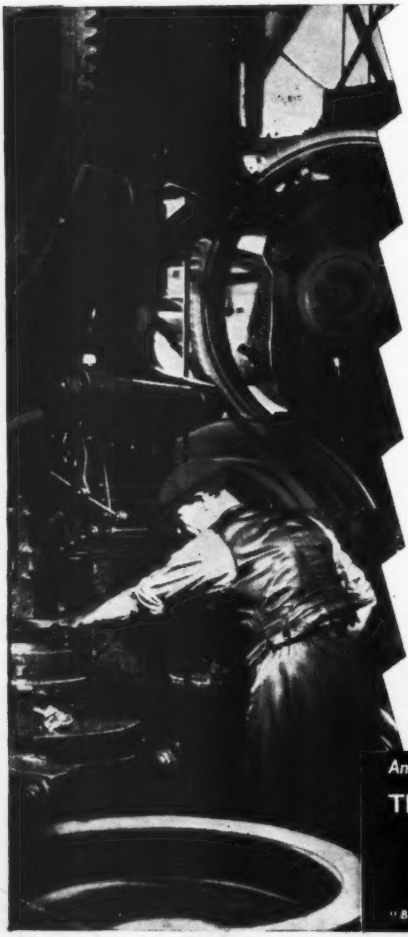

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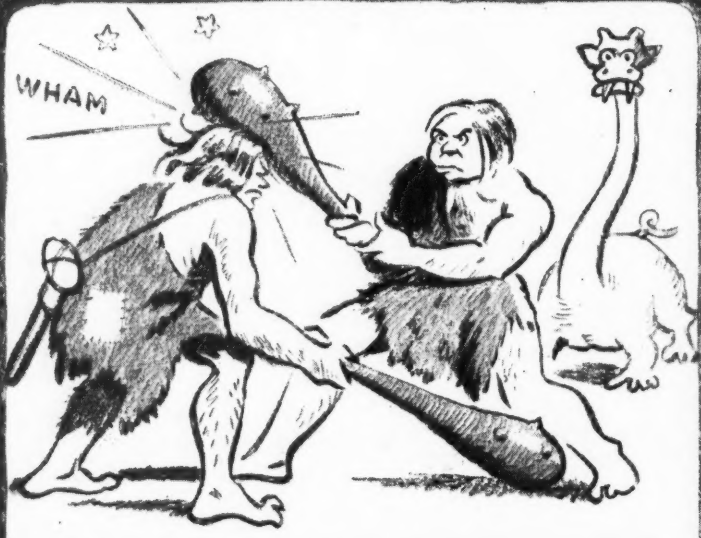

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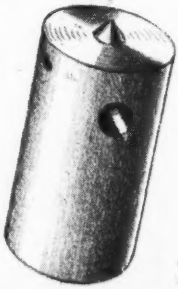

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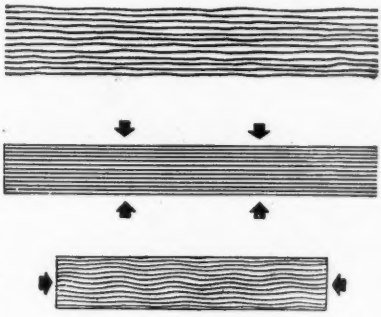

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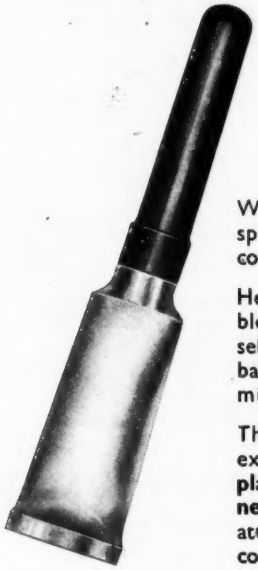

Where team work is necessary, the finest specialist in the world is useless—unless he co-operates with his co-workers.

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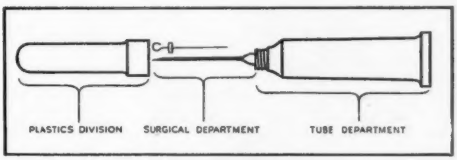
The total output of this container is taken up by Messrs. Burroughs Wellcome & Co. for their "MONOJECT" Ampoule Syringe.



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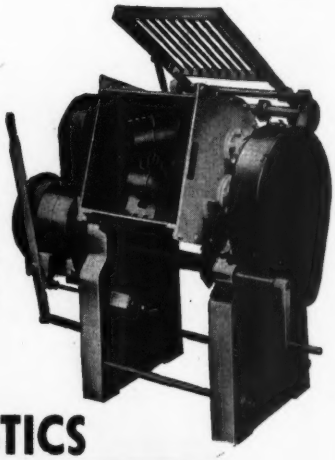

For many years custom has held that a super-stir operated by mixer blades of novel shapes must necessarily constitute a mix. The cold, hard fact is that it does nothing of the sort. A true homogeneous mix can only be obtained by scientifically designed inter-meshing mixer blades, such as those of the Beken Duplex Mixer. And when it is realised that this perfect mixture is obtained more speedily and at lower operating cost with the Beken Duplex Mixer, it is not surprising that it is replacing existing machines all over Great Britain. There are models specially suitable for the mixing of rubber doughs with pigments, spirits, etc.; may we send you particulars?

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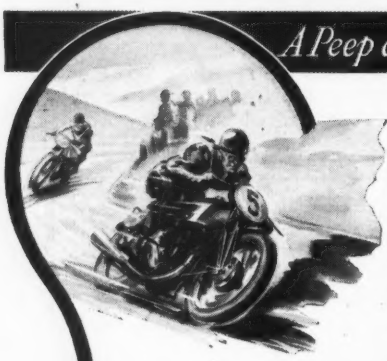

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"... and hundreds of spectators are lining the Manx roads for the Tourist Trophy International. Stanley Woods has just been checked in at Craig-ny-Baa, coming down the mountain road at ninety-odd, and looks the likely winner again." Who doesn't remember the broadcasts?

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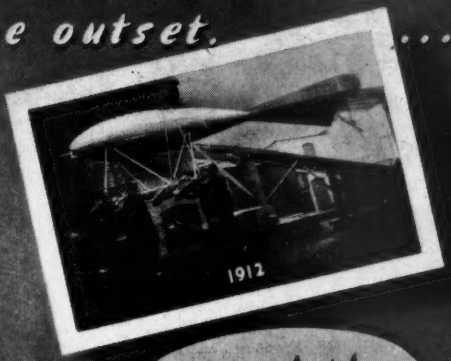

Yes! Monocoque construction and tricycle undercarriage in 1912! Continuous research and development since that time have enabled us to introduce numerous applications of laminated plastics, of which propeller blades, jigs and tools are but examples.

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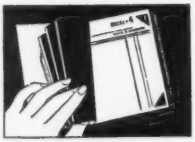

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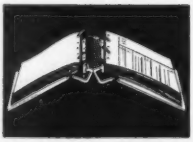

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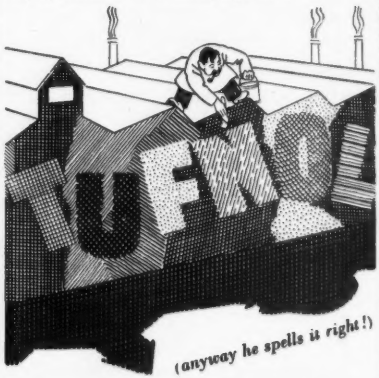

(anyway he spells it right!)

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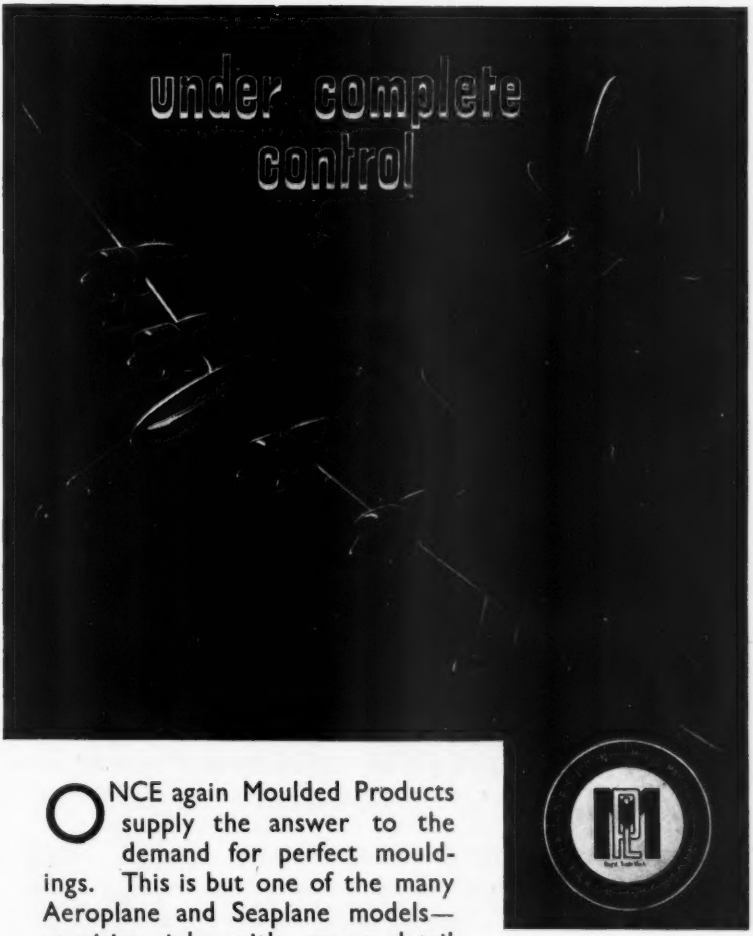

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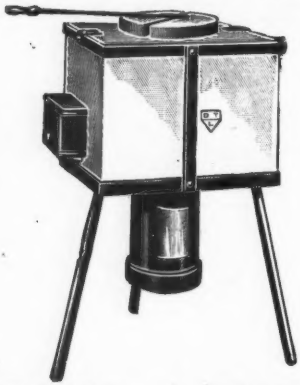

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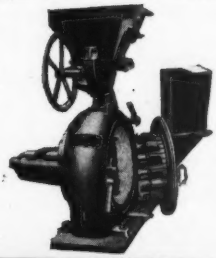

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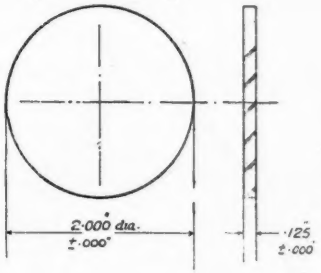

"WE REGRET, SIR, THAT WE CANNOT UNDERTAKE THE JOB."

It will pay you to *learn* the facts. It has always paid us to *tell* the truth. As Specialists with over 44 years' experience in the progressive development of the Plastics Industry, we maintain our reputation for precision work of the highest quality.

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TYRES are scarce—so remember never to brake suddenly unless in the gravest emergency. Apart from wear and tear to tyres remember, too, that sudden braking puts a colossal strain on your brake lining. Imagine the *destroying* heat that is generated within the brake drum. To stand up to these conditions, it was vital to discover a material which would irrevocably bond the asbestos strips that form the brake-lining. Isn't it significant that Bakelite Cement is chosen to-day for this purpose? Just another instance of the inevitability of Bakelite Plastics for a specific purpose. Most forms of Bakelite Plastics are only available to-day for priority use and our wartime experience has taught us much which manufacturers in many industries can turn to good account when we are able once more to tackle peacetime problems.

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TREFOIL

BAKELITE PLASTICS

REG'D. TRADE MARKS

Pioneers in the Plastics World

16R

Vol. VII. No. 76 SEPTEMBER, 1943

Plastics

Dealing with the Manufacture, Uses and Potentialities of Plastic Materials

Proprietors - - TEMPLE PRESS LIMITED
Managing Director - ROLAND E. DANGERFIELD

Editor - M. D. CURWEN, B.Sc., A.I.C.
Offices - Bowling Green Lane, London, E.C.1

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NOTICES

All instructions, matter and passed proofs for all kinds of advertisements must reach the Head Office of "PLASTICS" by the 24th of each month to ensure insertion in the following month's issue.

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More than ever is paper waste required for our war industries. Waste paper makes munitions in a hundred forms—from shell cases to aeroplane parts.

The fact that goods made of raw materials in short supply because of war conditions are advertised in this journal should not be taken as an indication that they are necessarily available for export.

EDITORIALS

In Retrospect

FOUR years of the most horrible war in human history still gives us no time to relax. Yet to us, whose life is spent in watching the wheels of industry go round with, so to speak, a bird's eye, it may be permitted to put down on paper some reflections as we look backwards.

We wonder whether once again the British will be accused of muddling through their wars. Whatever the verdict we believe that the plastics industry will come out of it all with a record as good as that of any armament industry.

Early in 1939 we were still dreaming out new designs for radio cabinets and motorcar dashboards, marvelling at the transparent acrylic resins that created so much stir in the new bomber gun turrets and in "see-how-it-works" advertising campaigns. The injection moulders were devising new, ingeniously cunning or amusing scent-bottle containers, tobacco firms were pondering over the proposed plastic cigarette cases for the Christmas trade. Electrical companies were just introducing new types of domestic heaters constructed entirely, except for the heating elements, of moulded resins. All the new pubs and cabarets were being fitted with lovely laminated table tops, counters and panels. The Scots Express had recently been supplied with its transparent plastic observation car and, with great secrecy, the greatest liner of all, the "Queen Elizabeth," had been fitted with 2,000 important units made in solid cast phenolic resin.

When war did come, the plastics industry seemed merely to change step or perhaps to make a half right turn. At least it seemed so to the general onlooker. Indeed this is not entirely strange for it is so constituted that there was in fact no fundamental change in operational machinery. The only change, taken by and large, it seemed, was in the type of object produced and therefore in the mould and that was merely a repetition of peace-time worries. To the worker within the industry it was not as simple as all that.

We had now new types of customers—the Navy, the Army and the Air Force—customers who made extraordinary demands in output, in quality and in tolerances, who introduced new difficulties with demands for new properties in powder, rod and sheet, who installed control by inspectors.

While peace-time manufacture sank to zero, war demands grew to enormous dimensions, and headaches accumulated through labour difficulties and labour dilution, new machinery allocations, the heart-breakingly slow production of moulds, the not unimportant matter of being bombed out of house and home, and the inevitable difficulties of raw material supply through growing demands.

Many even in the plastics industry itself did not realize the number of threads in the whole skein. Expansion of a phenolic resin factory means expansion in coal distillation, an increase and dispersion of formaldehyde factories, an increase in intake and training of young chemists. Without alcohol our polythene production is endangered so that our supplies of molasses for fermentation must be ensured. Laminated material manufacture entails a chain of sequences taking place in Canada, U.S.A., and Australia via Lancashire or Yorkshire. Similarly, those outside the moulding industry know little of what the modern precision mould means, of high-grade steel, of copper-beryllium production, of machining, grinding and plating.

All these threads and more—the uniting of the individuals in the industry into one cohesive whole, the liaisons between the

Services and the manufacturing units—had to be gathered together and woven into the battle-dress fabric which the plastics industry now wears.

How strong it is we shall one day be able to tell. There is every reason to be proud of it. And if we may point to two organizations that have been mainly responsible for its structure, it is to the British Plastics Federation and to Plastics Control. They have indeed done well for us.

So it is that after four years of war the plastics industry stands full grown, very strong and established as a producer of fine tools for the fighting man.

Some years ago we said that the plastics industry would reach its next milestone (the first had been its entry into the electrical industry) when its products had been accepted by the engineer. That milestone has now been passed and we are moving on.

X-Ray Examination of Plastics

IT has been said that one can evaluate the stature of an industry by the number of scientific instruments employed in the manufacture and in the examination of the final products. This is a modern truism.

However this may be, it needs but little thought to convince ourselves that the future of the plastics industry as producers of precision mouldings is bound up with an increasingly close control of its products. Indeed, as we have already declared in these pages, quality control in moulding factories rarely goes beyond a visual examination for large flaws by the human eye subject to the strains and worries of modern life. Chemical examination for degree of curing is rare. Physical testing is almost unknown.

It is pleasing to note, therefore, the interest aroused by certain fabricators in the application of X-ray examination of plastic mouldings. Indeed, some few X-ray apparatuses have already been installed and are being used with effect.

The plastics industry is logically more important as a field for X-ray work than even the metal industry. Since, in many respects, plastics and metals are indissolubly married and both are opaque to the eye, some method of determining the position of metal inserts or other additions must be available if we are to make products to rigid specification. In the electrical industry where almost all mouldings or extrusions contain conducting wires, metallic threads and screws their exact location and condition should be an essential part of fabrication. In the field of plastics reinforced with metal rods, strips or mesh, such control is also important.

Again it is common knowledge that internal flaws, cracks, blow-holes and other faults, due to incorrect conditions, can be discovered by no other means. The accidental inclusion of foreign matter such as small pieces of wire or mineral matter, not so rare as one would hope, can also be readily and rapidly detected.

The application of X-rays is not confined to these practical fields in the works itself. There is just as important a one in the investigation of flow of powders and in the segregation of pigments and fillers in powder mixtures, in the study of the flow of thermoplastics during extrusion and injection, processes thus affecting design of moulds, and probably even in the control of impregnation.

The industry is now ripe for more scientific control. In our October issue we shall re-open the subject by the publication of an introductory article by a well-known X-ray technologist.

Protection of Plastics

(During Handling and Transport)

MANY years ago, when rubber was a commodity made in Great Britain and when latex first appeared as a transportable commodity, we had the rather obvious idea that valuable goods, especially those that were easily broken, scratched, tarnished or otherwise spoiled could be rapidly dipped and coated with a protective layer of rubber by the then fairly new electro-depositing method. We

had visions of the completely safe transport of valuable porcelain, antique objets d'art, including paintings and even furniture, resisting the best endeavours of our railway porters, cutting down bulky packing, and finally cutting down high rates of insurance. On reaching the final destination, the rubber protective skin could be peeled off like a tangerine skin, leaving the object in its pristine beauty.

It was a pleasing idea and, we think, a useful one, shared most probably by many others who had any close acquaintance with rubber latex. We did not follow it to any conclusion, since it entailed an organization of a special type. However this may be, the need for such protection is necessary, although, perhaps, by simpler means.

There are, too, many other industries where protection of delicate objects during transport and, what is more important, during fabrication, is a vital necessity. This has long applied to the lens- and prism-making industry, where the surface of glass must be protected during grinding and similar operations. The surface may be protected by providing a linen cover or alternatively a plastic film such as is obtained by spraying and dipping in a cellulose lacquer film. The first is a cumbersome and time-costly job, while the second, although efficient, entails the use of solvents such as benzole, acetone, etc. Similar solvents must be used to remove the protective film.

With the advent of the plastic lens or delicate structure made of methyl methacrylate, polystyrene or cellulose acetate, the same condition of necessity for protection arises, for they are easily spoiled by careless handling. But we are faced here with the difficulty that solvents such as are described above cannot be used, because of attack on the basic plastic.

It is, therefore, interesting to note that a new resin soluble in ordinary white spirit (petroleum base) is now available. This means that a lens, for example, may be dipped in a solution of the resin in white spirit, so that after one hour, when the solvent has evaporated, it is coated with the resin, when grinding of the lens or other manipulation may be carried out safely. When the grinding operation is complete, the object is placed in white spirit, when the resin is removed.

Since white spirit does not attack the plastic surface, the new method introduces a safe means of protection.

Advisory Panel on Wood

The Ministry of Aircraft Production has recently set up an "Advisory Panel on the Application of Wood in Aircraft Construction." The terms of reference of the panel are:—

"To advise the Ministry of Aircraft Production on all matters relating to the use of wood in aircraft, with the following objectives:—

(1) Improving the quality of wooden aircraft and components.
(2) Aiding production by technical improvement of processes.
(3) Making the most effective use of the available timber.
(4) Improving the quality of glues."

The membership of the panel consists of the following representatives:—

Chairman: W. Hardy (R.D.Mat.).

M.A.P.: L. R. Logan, L. C. Whitchurch, J. M. Gray.

Secretary: E. Reeve Angel.

Plywood Manufacturers: H.P. Martin (Flexo Plywood Industries).

Wood Aircraft Design Firms: C. Chapleo (Airspeed (1934), Ltd.); G. A. Emery (Phillips and Powis, Ltd.); A. W. L. Calder (de Havilland).

Wood Veneer Moulders and Manipulators: A. E. Lain (Harris Lebus, Ltd.); H. A. Renn (Renn's Shaped Plywood, Ltd.); S. Smith (S. Smith and Co.).

Forest Production Research Laboratory: W. A. Robertson.

R. A. Establishment: Dr. W. D. Douglas.

British Plastics Federation: Dr. W. Blakey (British Industrial Plastics, Ltd.).

Aircraft Plastics Main Technical Committee: Dr. A. Caress (I.C.I. (Plastics).

Plastics in STRUCTURAL ENGINEERING

A Comparison is Made Between the Structural Properties of a Plastic of the Laminated Veneer Type and Those of AZM Magnesium Alloy, Duralumin and a Typical Grade of Mild Steel

By LESLIE P. DUDLEY, D.F.H., A.M.I.E.E., A.R.Ae.S.

INTRODUCTION

IN the case of the majority of engineering materials, some indication of their suitability for structural purposes is afforded by the magnitude of the tensile strength/specific-gravity ratio, but errors arise if this ratio be accepted too liberally, as an indication of the structural possibilities of a plastic material.

After tensile strength, elastic modulus is usually the next most important property of a structural material, and, with most classes of materials, a high value of the one property is accompanied by a high value of the other. In the case of plastics, however, a high tensile strength may be accompanied by a comparatively low elastic modulus or vice versa. Further, some plastics which appear, from a list of their properties, to be eminently suitable for structural purposes, cannot yet be fabricated in the requisite forms. For example, consideration of their tensile strength/specific gravity ratios tends to indicate polyamides of the nylon type as the most suitable group of plastics for structural purposes, tensile strengths up to approximately 50,000 lb./sq. in. being obtainable, with a specific gravity of about 1.1. This high value of tensile strength is, however, conferred by cold-drawing, and a satisfactory method of cold-drawing nylon in forms other than monofilaments still awaits development. Meanwhile, it occurs to the author that, particularly where pure tensile stresses are involved, there may be some future for members comprising a multiplicity of drawn filaments embedded in a suitable bonding medium.

From the foregoing it will be evident that before deciding to adopt a particular plastic for a given structural application, full consideration should be given to all the factors involved. Not only must the physical properties of the material be adequate to meet the specified loading conditions but, in addition, it is necessary to be sure that the material in question is suitable for use under the particular conditions of humidity, temperature, etc., which will prevail in the vicinity of the structure. It is easy to see that in some cases the most satisfactory structure may result from the use of several different plastics, the material for each class of member being selected in accordance with the duty which it is to perform.

At the present stage of development of the plastics industry the materials which appear to offer the greatest promise of success for structural purposes are laminated phenol-formaldehyde, compressed wood and bonded plywood. The properties of such products vary over a wide range according to the nature of the laminating material used, the laminating conditions, the type of resin and the resin content. With phenol-formaldehyde laminated paper, for example, tensile strengths of 10,000 to 30,000 lb./sq. in. are obtainable, depending upon the type of paper used and the resin content. Much higher values may be obtained by the use of special fibres.

It is intended in the present paper to examine the properties of sections composed of laminated $\frac{1}{16}$-in. birch veneers in comparison with the properties of equivalent sections in other structural materials. The materials with which the plastic will be compared are AZM magnesium alloy, duralumin and a typical mild steel.

PART 1.—(a) Tensile Loading

The physical properties of a plastic of the type with which we shall be concerned herein may be taken as being very approximately as follows:—

Resin content	20%
Ultimate tensile strength	17.4 tons/sq. in.
Ultimate compressive strength	8.0 tons/sq. in.
Elastic modulus	2.0×10^6 lb./sq. in.
Shear strength, parallel to plane of lamination	1.6 tons/sq. in.
Shear strength, at right angles to plane of lamination	0.71 tons/sq. in.
Specific gravity	0.95

We will first compare the relative cross-sectional areas and weights per unit length of four structural members designed to withstand the same axial tensile load, one of the members being composed of a plastic having the above properties and the other three of AZM magnesium alloy, duralumin and mild steel. In view of the fact that the plastic exhibits no definite elastic limit or proof stress, it will be assumed that the four members are to possess the same factor of safety, based on the ultimate strengths of the materials. In actual practice the factors of safety adopted would not all be the same, but it is considered justifiable to neglect this fact in the present instance in order to facilitate the comparison. It should, perhaps, also be mentioned in passing that in a previous paper[1] a similar comparison was made between three equivalent members of AZM alloy, duralumin and steel, but in that case the calculations were based on proof stresses, consequently the relative figures given for the three materials differ from those indicated below.

The ultimate strengths of AZM alloy, duralumin and mild steel respectively may be taken as 20.3, 25 and 27.5 tons/sq. in. and the specific gravities as 1.80, 2.79 and 7.84.

For a given load the necessary cross-sectional area will clearly be inversely proportional to the ultimate tensile strength. Moreover, the weight per unit length will vary directly as the specific gravity divided by the ultimate tensile strength. Let us, therefore, denote the cross-sectional area and weight per unit length of the steel member by respectively A and W; then, adopting the constants given in the previous paragraph, we may derive the relative values indicated in Table 1. Consideration of the results shows that adoption of a tie of the plastic material has the effect of reducing the weight by about

Table 1.

Material	Area	Weight
Plastic	1.58A	0.19W
AZM alloy	1.35A	0.31W
Duralumin	1.10A	0.39W
Steel	A	W

81 per cent. of that of the equivalent steel member, 51 per cent. of that of the equivalent duralumin member or 39 per cent. of that of the equivalent member in AZM alloy.

(b) Compression Loading

When subjecting a specimen section of a structural material to a compression test in order to determine its ultimate strength, caution must be observed in deciding upon the length of the sample to be tested. If the specimen be very short, block action may take place. A discussion of this phenomenon is, however, outside the scope of the present article; it will suffice for our purpose to note that such action frequently causes very short specimens to exhibit compressive strengths which are much higher than would be anticipated from consideration of the nominal characteristics of the material. If, on the other hand, the specimen be too long, column action

will result.[2] That is to say, failure will occur through bending at a lower load than that required to cause rupture by pure compression.

Complication will be avoided if we assume in the present discussion that the struts considered are of such proportions that neither of the above factors are operative. Under these circumstances the results obtained must be interpreted as applying only to compression members having slenderness ratios between the very approximate limits of 5 and 15.

The ultimate compressive strength of laminated $\frac{1}{16}$-in. birch veneers may be taken as approximately 8.0 tons/sq. in., as already indicated. In the case of AZM alloy, compression tests have shown that an ultimate strength of some 22.8 to 26 tons/sq. in. is obtainable, so we shall be justified in adopting the mean value of 24.4 tons/sq. in. for the present purpose.

For duralumin, as for the majority of aluminium alloys, the ultimate compressive and tensile strengths are substantially

Table 2.

Material	Area	Weight
Plastic	3.44 A	0.42 W
AZM Alloy ..	1.13 A	0.26 W
Duralumin ..	1.10 A	0.39 W
Steel	A	W

equal, so the value of 25 tons/sq. in. may again be assumed. Likewise, for many grades of mild steel the ultimate strength in compression is equal to that in tension. Hence, the value of 27.5 tons/sq. in. employed in (a) above may be used in this case also.

Utilizing once again the well-known relationship, $f = \frac{P}{A}$, and tabulating the results, we obtain the relative values given in Table 2. As will be evident, the plastic compares less favourably with the other materials in this instance than in the previous case. Although the weight is about 58 per cent. less than that of the equivalent steel strut, the necessary cross-sectional area is much greater.

PART 2.—Transverse Loading

Elsewhere[1] the author has indicated some of the reasons in favour of designing transversely loaded members or beams expressly for the particular loading conditions involved. In the majority of practical cases, nevertheless, economic considerations prohibit adherence to this ideal procedure and render it necessary to adopt a compromise. That is to say, after the required dimensions for a given member have been determined, it is then usually necessary to select a suitable member from an existing range of standard sections. Most such sections are, in themselves, compromises in that they are not designed to give maximum efficiency under one particular set of loading conditions but rather to provide a fair degree of efficiency under diverse conditions. Except for a limited range of special shapes, standard I-sections, for example, are not designed exclusively for use as beams under loads acting at right angles to the flanges, as they may be required to support loads applied parallel to the flanges, axial loads or compound loads.

Having regard to the above considerations, it is evident that our present purpose will be best served by comparing geometrically similar beams, i.e., beams having identical relative cross-sectional proportions. The cases which will be considered are, first, that of beams capable of supporting the same load under identical conditions, and, secondly, that of beams exhibiting equal deflection under the same loading conditions.

(a) Beams of Equal Strength

Consider a beam, of section modulus Z, and let M denote the bending moment acting upon the member. The maximum stress in the extreme fibres will then be given by—

$$f = \frac{M}{Z}$$

Adopting the suffixes s, a, m and p to denote respectively steel, duralumin,

AZM alloy and the plastic, it is clear that we require the following conditions to be satisfied:—

$$\frac{M}{Z_s} = 27.5k;\ \frac{M}{Z_a} = 25k;\ \frac{M}{Z_m} = 20.3k;\ \frac{M}{Z_p} = 8k$$

where k is a constant and the multipliers represent the ultimate strengths of the materials in tons/sq. in. In the case of AZM alloy the tensile strength is lower than the compressive strength, and, in consequence, the value of the former property must be adopted in this instance. It is worth noting, however, that were our calculations based on the proof stresses of the materials, it would be necessary to adopt the compressive value as this amounts only to about 8.9 tons/sq. in. as compared with some 15.3 tons/sq. in. obtainable in tension.

From the four relationships given above it is evident that—

$$\frac{Z_a}{Z_s} = \frac{27.5}{25.0},\ \frac{Z_m}{Z_s} = \frac{27.5}{20.3} \text{ and } \frac{Z_p}{Z_s} = \frac{27.5}{8.0}$$

$$\text{Hence } Z_a = 1.10Z_s \quad .. \quad .. \quad (1)$$

$$Z_m = 1.36Z_s \quad .. \quad .. \quad (2)$$

$$\text{and } Z_p = 3.44Z_s \quad .. \quad .. \quad (3)$$

It is readily demonstrable that, in the case of geometrically similar members, the section modulus varies directly as the cube of any linear cross-sectional dimension. Consequently, denoting some such dimension by d, from (1) it follows that—

$$d_a^3 = 1.10d_s^3$$

$$\text{or } d_a = 1.032d_s \quad .. \quad .. \quad (4)$$

Similarly, from (2) we have—

$$d_m^3 = 1.36d_s^3$$

$$\text{or } d_m = 1.108d_s \quad .. \quad .. \quad (5)$$

and from (3)—

$$d_p^3 = 3.44d_s^3$$

$$\text{or } d_p = 1.510d_s \quad .. \quad .. \quad .. \quad (6)$$

showing that, in adopting one of the alternative materials in place of steel, we must multiply the cross-sectional dimensions by respectively 1.032, 1.108 or 1.510 according to whether duralumin, AZM alloy or the plastic is to be used.

We may also write down the relative weights of the beams in the forms—

$$\frac{W_a}{W_s} = \frac{2.79 \times 1.032^2}{7.84} = 0.38$$

$$\frac{W_m}{W_s} = \frac{1.80 \times 1.108^2}{7.84} = 0.28$$

$$\text{and } \frac{W_p}{W_s} = \frac{0.95 \times 1.510^2}{7.84} = 0.28$$

thereby bringing to light the interesting fact that an approximately equal weight saving, amounting to some 72 per cent., results from the use of either the magnesium alloy or the plastic, compared with a saving of about 62 per cent. obtainable by using duralumin.

Let us now compare the relative deflections of the four beams under similar loading conditions. From first principles we know that the deflection of a beam is inversely proportional to the product of the elastic modulus of the material and the moment of inertia of the section, that is—

$$\delta \propto \frac{1}{EI}$$

It is also known that the moment of inertia varies directly as the fourth power of any linear cross-sectional dimension. Hence, adopting the same suffixes as before, we may write—

$$\frac{\delta_a}{\delta_s} = \frac{E_s d_s^4}{E_a d_s^4} \quad .. \quad .. \quad .. \quad (7)$$

$$\frac{\delta_m}{\delta_s} = \frac{E_s d_s^4}{E_m d_m^4} \quad .. \quad .. \quad .. \quad (8)$$

$$\text{and } \frac{\delta_p}{\delta_s} = \frac{E_s d_s^4}{E_p d_p^4} \quad .. \quad .. \quad .. \quad (9)$$

The elastic moduli of the materials with which we are concerned may be taken as approximately 10×10^6 lb./sq. in. for duralumin, 6.7×10^6 lb./sq. in. for AZM alloy, 2×10^6 lb./sq. in. for the plastic, and 30×10^6 lb./sq. in for steel. Substituting the appropriate values in the above equations, from (7) we obtain—

$$\frac{\delta_a}{\delta_s} = \frac{30 \times 10^6}{10 \times 10^6 \times 1.032^4} = 2.64$$

Similarly, (8) becomes—

$$\frac{\delta_m}{\delta_s} = \frac{30 \times 10^6}{6.7 \times 10^6 \times 1.108^4} = 2.98$$

and from (9) we have—

$$\frac{\delta_p}{\delta_s} = \frac{30 \times 10^6}{2 \times 10^6 \times 1.510^4} = 2.88$$

As will be evident from the above results, whilst there is no great difference between the deflections exhibited by the duralumin, AZM alloy and plastic beams, the deflections are considerably greater than that resulting from the use of a steel member of equal strength. In the case of the plastic member, the assumption has been made that the load is applied in a direction parallel to the plane of lamination. A greater deflection would, of course, result from application of the load at right-angles to that plane.

We will now compare the relative characteristics of the four beams if they be designed to give the same deflection under a given load.

(b) Beams of Equal Stiffness

For equal deflection under identical loading conditions it will be understood that we must have—

$$E_s I_s = E_a I_a = E_m I_m = E_p I_p$$

which may be rearranged to provide the equations—

$$I_a = \frac{E_s I_s}{E_a} = \frac{30 \times 10^6 I_s}{10 \times 10^6} = 3.0 I_s \quad .. \quad (10)$$

$$I_m = \frac{E_s I_s}{E_m} = \frac{30 \times 10^6 I_s}{6.7 \times 10^6} = 4.48 I_s \quad .. \quad (11)$$

$$\text{and } I_p = \frac{E_s I_s}{E_p} = \frac{30 \times 10^6 I_s}{2 \times 10^6} = 15.0 I_s \quad .. \quad (12)$$

But it is well known that the moments of inertia of geometrically similar beams are directly proportional to the fourth power of any linear cross-sectional dimensions, that is to say—

$$I \propto d^4$$

Accordingly, from (10), (11) and (12) respectively it follows that—

$$d_a^4 = 3.0 d_s$$
$$\text{or } d_a = 1.317 d_s$$

$$d_m^4 = 4.48 d_s$$
$$\text{or } d_m = 1.455 d_s$$

$$\text{and } d_p^4 = 15.0 d_s$$
$$\text{or } d_p = 1.968 d_s$$

from which we see that in this case changing from steel to one of the lighter materials necessitates multiplying the cross-sectional dimensions by 1.317, 1.455 or 1.968, depending upon whether it is decided to adopt duralumin, AZM alloy or the plastic.

The weight relationships in the present instance amount to—

$$\frac{W_a}{W_s} = \frac{2.79 \times 1.317^2}{7.84} = 0.62$$

$$\frac{W_m}{W_s} = \frac{1.80 \times 1.455^2}{7.84} = 0.49$$

$$\text{and } \frac{W_p}{W_s} = \frac{0.95 \times 1.968^2}{7.84} = 0.47$$

from which we see that, although the greatest weight saving results from use of the plastic member, the saving is considerably less than that obtainable in the case of beams designed for equal strength.

Let us compare the relative strengths of the beams at present under discussion. We know that the section modulus is proportional to the cube of any cross-sectional dimension, thus—

$$Z \propto d^3$$

Hence the relative strengths may be expressed in the convenient forms—

$$\frac{F_a}{F_s} = \frac{1.317^3 \times 25}{27.5} = 2.08$$

$$\frac{F_m}{F_s} = \frac{1.455^3 \times 20.3}{27.5} = 2.28$$

$$\text{and } \frac{F_p}{F_s} = \frac{1.968^3 \times 8}{27.5} = 2.22$$

which show that in each case the strength of the light metal or plastic beam is more than twice that of the steel member.

For convenience in comparing the results, the relative characteristics of the several beams which we have discussed are displayed in Table 3. Consideration of these results and also of those given in the earlier tables leaves no doubt that a useful field of application for many structural purposes awaits plastics of the laminated veneer type.

Appendix

Whilst it is likely that the great majority of readers will have a knowledge of the characteristics and structural properties of mild steel, it is possible that some will welcome a few words concerning the other two metals entering into the foregoing discussion.

Duralumin

Aluminium in the pure state possesses excellent ductility and—depending upon

Table 3.

No.	Material	Area	Weight	Deflection	Strength
1	Plastic	2.28 A	0.28 W	2.88 δ	F
2	AZM Alloy	1.23 A	0.28 W	2.98 δ	F
3	Duralumin	1.07 A	0.38 W	2.64 δ	F
4	Steel	A	W	δ	F
5	Plastic	3.88 A	0.47 W	δ	2.22 F
6	AZM Alloy	2.12 A	0.49 W	δ	2.28 F
7	Duralumin	1.73 A	0.62 W	δ	2.08 F

Nos. 1, 2, 3 and 4: Equal strength. Nos. 4, 5, 6 and 7: Equal stiffness.

the degree of purity—resistance to corrosion by the atmosphere and by a large number of the chemicals used in industry. Indeed, by virtue of the above properties, pure aluminium is unsurpassed by any other metal for many purposes. Low mechanical strength, however, renders pure aluminium unsuitable for structural purposes, except in rare cases in which very small stresses are involved. Hence, with the aid of small additions of other metals, such as copper, zinc, etc., high-tensile alloys have been evolved, these alloys possessing several times the strength of pure aluminium with practically the same specific gravity.

The density of commercially pure aluminium is approximately 0.098 lb./cubic in., and the proof stress of this material, in the fully annealed condition, is only about 4,000 lb./sq. in. In the case of the wrought alloys used for structural work, additions of other metals, together with suitable heat treatment, enable the proof stress to be raised to some 50,000 lb./sq. in. The densities of such alloys vary between the approximate limits of 0.096 and 0.101 lb./cubic in., so we see that in some cases they are even less than that of pure aluminium. It is a remarkable achievement in the science of metallurgy to have produced a range of materials exhibiting such widely differing mechanical properties with so small a variation in weight.

Methods of manufacturing structural components in aluminium alloys vary not only with the type of alloy but also with the nature of the commodity to be produced. Sheet and plate, and frequently bar, rod and structural sections are produced by rolling. Heavy-gauge plate and also sections having thick scantlings are flattened and straightened by rolls. For the straightening of light-gauge plate, sheet and certain sizes of sections, stretching is customarily employed.

An endless variety of sections is obtainable by the extrusion process, in which metal is forced through an orifice possessing the same shape as the desired section. By this means sections having a major dimension of about a foot have been produced, but, as a general rule, extrusion is confined to the production of sections of appreciably smaller size.

Drawing is employed for the production of seamless tubing in a wide range of aluminium alloys, and, from certain alloys, excellent forgings can be made.

From the point of view of the structural engineer, duralumin is undoubtedly one of the most important alloys. Some of the chief structural properties of this material have already been given in the present paper, so it will suffice to add here that the chemical composition is approximately as follows:—94.5 per cent. Al, 4 per cent. Cu, and about 0.5 per cent. each Mg, Mn and Fe. As is well known, this alloy is used extensively in aircraft construction, not only in the forms of tubes and sections, but also in the form of sheet for covering the wings

and fuselage. Such aircraft "skins," however, are usually of a special composite form known as Aldural (manufactured by James Booth and Co. (1915), Ltd.). This product consists of a sheet of duralumin faced on each side with a thin layer of high-purity aluminium. Each of these two layers possesses only about 5 per cent. of the thickness of the duralumin core, resulting in a composite sheet combining the excellent corrosion resistance of pure aluminium with the high strength of duralumin.

Apart from its numerous uses in aircraft construction, duralumin is also employed extensively in the manufacture of vehicles and containers for both road and rail transport, for long built-up crane booms, for mobile fire-escape ladders and a host of other purposes where both strength and lightness are required.

AZM Alloy

Magnesium, as in the case of aluminium, is comparatively soft in the pure state and possesses only a low mechanical strength. Hence, in this form, it is of little value as a structural material. Again, as in the case of the aluminium industry, however, research chemists and engineers have succeeded in evolving a series of alloys exhibiting excellent mechanical properties without raising the specific gravity of the material appreciably above that for pure magnesium.

The most useful of the alloying constituents employed at the present time are, in order of importance, aluminium and zinc, the primary function of the former being to improve the tensile strength, and of the latter to enhance the elongation.

Between the years 1923 and 1927 P. Spitaler[3] conducted a series of interesting tests on a number of experimental binary Mg-Al alloys. Tests were carried out on both sand-cast and extruded samples. In the case of the sand-cast specimens it was found that the tensile strength rose steadily with each increase in the aluminium content, reaching a maximum with a content of approximately 6 per cent. (by weight). Additions of aluminium beyond this figure produced a marked decrease in strength. In the case of the extruded samples the effect was found to be less clearly defined, maximum tensile strength resulting from an aluminium content of about 10 per cent

With regard to the effect of zinc additions, inclusion of a given percentage of this metal produces a smaller increase in strength than that resulting from addition of the same percentage of aluminium. For this reason it is not usual to employ binary Mg-Zn alloys; zinc is of much greater utility as a constituent of ternary Mg-Al-Zn alloys wherein its principal function is to improve the elongation, as already indicated. Of the various wrought alloys in this class, that known as AZM and used for comparative purposes in the present article, is certainly one of the most useful light metals available to the structural engineer. Composed of approximately 93 per cent. Mg, 6 per cent. Al and 1 per cent. Zn, it possesses properties comparable with many of the high-strength aluminium alloys. Just as there is ample scope in the industry for the healthy development of both aluminium-base and magnesium-base alloy structural members, so also, no doubt, will the near future show that there are a multitude of fresh fields awaiting the full maturity of plastic members.

In conclusion, the author wishes to express his indebtedness to Messrs. I.C.I. (Plastics), Ltd., for much valuable information provided in connection with plastics of the laminated veneer type. His thanks are also due to Messrs. James Booth and Co. (1915), Ltd., and the British Aluminium Co., Ltd., for permission to publish this article.

REFERENCES

(1) *"Light Metals," April, 1943. "Magnesium Alloys in Structural Engineering," L. P. Dudley.* **(2)** *"Light Metals," Dec., 1941. "Ultimate Strength of Duralumin Compression Members," L. P. Dudley.* **(3)** *"The Technology of Magnesium and its Alloys," translated from the German by F. A. Hughes and Co., Ltd., and Magnesium Elektron, Ltd.*

INQUIRIES AND ANSWERS

(In Which is Included General Correspondence)

IMPORTANT NOTICE: If inquirers wish to receive replies by post, a stamped and addressed envelope must be included in their letter. Unless otherwise stipulated, it is understood that the submission of a problem to the Editor permits its publication in this journal.

Thermoplastic Cables

Recently there have been many articles and statements in the Technical Press regarding Thermoplastic Cables. It appears to my Committee that these publications are tending to overlook the war emergency background against which Thermoplastics in general and P.V.C. compounds in particular are being introduced into general cable manufacture, and it is felt that publicity should be given to the following considerations:—

(i) The major problem with which the Cable Industry is faced at this juncture is the maintenance of supplies of cables vital to the war effort in the absence of adequate supplies of various materials hitherto considered essential.

(ii) The overwhelming bulk of the Industry's production is of cables for the Services. Of these quite a large proportion are short-life cables in the sense that, under war conditions, the circumstances in which they are used drastically limit their expectation of life.

(iii) The first of these factors assign to Thermoplastics the major role of saving rubber (including synthetic rubber); the second, coupled with the limited choice of polymers, plasticizers, and extenders available under war conditions, determines the technical policy under which Thermoplastic compounds are introduced for that purpose and renders of secondary importance their development for meeting the wide variety of potential uses in general industrial and domestic wiring.

Thus, in the case of P.V.C., which is the principal Thermoplastic material involved, these considerations have led to the necessity for standardizing the compounds employed and limited their number to the minimum dictated by Service needs. In so far as these compounds are suitable for cables for general wiring, they are admitted under an amendment of B.S.7, but the preliminary nature of this step will be clear from the foregoing, and until further progress is made with development work in this field—and it is being given as much attention as wartime conditions permit—P.V.C. cables should not be used indiscriminately.

The present position may, therefore, be summarized by saying that, as substitutes for war emergency rubber cables for general wiring work, P.V.C. cables and flexibles will give satisfactory service under most conditions, and in that sense they must be utilized to the maximum possible extent in the national interest. Where, however, conditions are thought to be arduous or otherwise unfavourable—e.g., where cables are to be installed under extreme conditions of temperature, the purchaser would be well advised to communicate with the Secretary, Cablemakers' (War Emergency) Technical Committee (a committee which represents from the technical standpoint the British Cablemaking Industry as a whole); address, Hamilton House, Victoria Embankment, London, E.C.4, from whom he can obtain unbiased advice as to the suitability of P.V.C. cables for the particular type of service involved.

W. BISHOP,
Chairman, Cablemakers' Planning Committee.

Clothing for Plastics

Would you kindly inform me if extra clothing coupons are available this year for workers in the plastics industry (e.g., hydraulic press moulders)?

My employer's manager states that he has no instructions regarding them.

Smethwick. B.G.W.

[EDITOR'S NOTE: You are quite correct in inferring that extra clothing coupons are available for workers in the plastics industry. The following schedule of coupon allowance has been devised:—

25 Extra Coupons:

Process worker-mixers, millmen, still operators, cast resin operators, sifters, grinders, weighers, pelleters, granulating, densifying, rolling.

Hydraulic and power press moulders.

Operators in formalin seasoning room.

20 Extra Coupons:

Maintenance fitter wholly engaged in maintaining plant producing plastics.

15 Extra Coupons:

Cementer, cellulose sprayer; sheet

(Continued on p. 407)

Fire Hazards in the Plastics Industry—I

A Treatise on Causation

By H. RONALD FLECK, M.Sc., A.I.C.

FIRES in industry cause havoc and destruction amongst valuable raw and finished materials and what is often irreplaceable plant. In peace such losses are bad enough. In war-time they aid the enemy. Many such industrial outbreaks are preventable provided both workers and management alike have a proper appreciation of the hazards and risks peculiar to their own industrial processes.

In attempting to resolve the problem of fire in the plastics industry, it will be necessary to reduce the whole matter to its basic conception of cause and effect. Upon achieving a technical analysis of causation, we shall then be equipped with that fore-knowledge which will enable us to engage upon an active defence against fire, one of the most rapacious enemies of industrial effort.

The Causes of Fires

Two main causes operate to produce fires. (a) Combustion induced by direct ignition with flame or sparks and (b) spontaneous ignition, possibly of some material which is not normally considered to be inflammable.

Ignition (of solids, as well as of gases and liquids) is best defined as the initiation of self-supporting and self-propagating combustion, with accompanying glow or flame. It is well known that combustion is a process of oxidation taking place at a highly accelerated rate, the energy of the exothermic reaction being manifested by the emanation of light energy.

In the case of solids, ignition is assured when the rate of heat production by oxidation of a given surface area begins to exceed the rate of loss of heat to the surroundings. The ensuing autogenous temperature rise then brings the material to the glow- or flame-point at a rate dependent on its coefficient of oxidation-acceleration with temperature, its exposed surface per unit weight, and the rate of oxygen supply or air renewal upon that surface.

This type of ignition is common in dust-laden atmospheres and will take place with materials which are not normally highly inflammable.

For example, a moulded plastic fabricated from a phenolic resin will not easily burst into flame by the application of heat, but when such a material is in a light fibrous form, in thin sections, or in a finely comminuted state its degree of ignitibility is very much greater than in the massive or compacted form.

Chemical Structure and Reactivity

Since chemical structure profoundly influences chemical reactivity, the structure of a particular substance will influence the rate of heat development on oxidation and hence the proneness to ignition of the particular material. It has been shown by research workers in America that substances having open chain structures are possessed of greater ignitibility than substances having closed chain or ring structures. Thus, petrol which contains mainly open chain compounds of the paraffinic type such as pentane, hexane and heptane would be expected to have greater inflammability than benzene or toluene which both have ring structures. This is confirmed by the experimental fact that the flash-point (closed cup) of petrol is −50 degrees F., whereas that of benzene is 12 degrees F. and of toluene 40 degrees F.

Other structural linkages and configurations have been shown to increase inflammability and in particular it has been noted that the ether or bridged linkage

of oxygen in the molecular structure tends to increase ignitibility. The existence of this linkage has been demonstrated in phenol-formaldehyde resins and, incidentally, in cellulose materials. It is possible, using an arbitrary but standard method of determining the ignition point, to list the material, and by taking this as a standard figure of 100 we find that absorbent cotton has an index of 140, paper pulp 145, phenolic resin (filled) 160, wood flour 165, cellulose acetate 175, and bitumen 200.

Polymers and Inflammability

A further factor now enters into the calculations. As molecular complexity increases, so chemical reactivity decreases. Hence, during the process of polymerization, i.e., during increasing complexity, ignitibility will decrease. As an example, styrene monomer which has a fairly low flash-point, ignites readily, but polystyrenes of fairly highly polymeric level ignite only with difficulty. At elevated temperatures, however, polystyrene is depolymerized to the monomer which then ignites readily. This constitutes further hazards, since temperatures insufficient to cause ignition of a polymer may be high enough to cause progressive depolymerization and subsequent combustion. A polymer may, therefore, smoulder unnoticed until suddenly it bursts into flame. The flash-points (closed cup) of liquids which are subsequently polymerized may be determined approximately by means of the formula:

Flash Point = (0.73 × I.B.P.) − 100

where I.B.P. is the initial boiling point.

Thus for vinyl acetate having an initial boiling point of 163 degrees F. we obtain a result of 18 degrees F., which is in agreement with the experimentally determined value. This formula holds for esters containing carbon, hydrogen and oxygen, but for hydrocarbons 122 must be subtracted instead of 100.

By determining the temperature at which depolymerization takes place and correlating this with the flash-point, it is comparatively simple to decide whether a particular polymer presents this hazard or not. Attention must be paid to the state of division of the polymer if it is solid.

Since we are equally concerned with fire risks due to volatile solvents used in processing, we must examine the concept of liquid and gas inflammability.

Ignition of gases and of liquids involves a direct attack of oxygen on molecular or near-molecular subdivisions, each surrounded by air, combustion reactions in gases probably being propagated by active particles of some sort (possibly some form of intermediate oxidation product), the diffusion of the particles being possibly as important as heat transfer.

Thus, in a dust-laden atmosphere, the probability of vapour ignition is vastly increased. The ease of evaporation of a solvent as exemplified by its flash-point is of primary importance in determining the ease of inflammability of that solvent. The following list shows the flash-points of various solvents and plasticizing liquids used in the plastics industry, arranged in an ascending order of flash-points (degrees F.):—

Petrol	−50
Carbon bisulphide ...	−22
Ether	−20
Acetaldehyde	−17
Acetone	0
Benzene	12
Vinyl acetate	18
Ethyl acetate	24
Toluene	40
Ethyl benzene	59
Alcohol	60
Xylene	63
Butyl acetate	72
Amyl acetate	76
n-Butyl alcohol	34
Styrene	90
Turpentine	95
Naphtha	100
Acetic anhydride ...	171
Formaldehyde	130
Phenol	175
Cresol	180
Nitrobenzene	190
Dibutyl phthalate ...	315
Castor oil	445
Tricresyl phosphate ...	460
Carbon tetrachloride ...	non-flam.

Thus many of the liquids used by the plastics industry are a potent source of danger even at temperatures round about freezing point.

Carbon bisulphide will even ignite when an electric lamp bulb is switched on some distance away from the liquid itself, particularly if the atmosphere is dusty.

Little is known of the mechanism of spontaneous combustion, except that it is undoubtedly connected with the autogenesis of heat by rapid oxidation reactions. It is a fairly well-known source of danger, particularly with vegetable oils showing incipient rancidity. Castor oil, used in the plastics industry as a plasticizer, is prone to ignite spontaneously, especially when exposed to the air on cotton rags and oily waste.

These theoretical considerations enable us to predict and guard against fire hazards. They are the result principally of chemical action and, chemical action, like any other action, is the result of definite causes. Having outlined these causes the next article will deal with effect, and the precautions which must be adopted if fire dangers in the plastics industry are to be minimized.

Plastics in South Africa

The South African Railways and Harbours Administration have placed an order for 15,000 plastic tumblers with a large Durban factory specializing in the manufacture of plastics. A director of the factory stated that when the material for the manufacture of the tumblers arrived it was intended that they should be put on the market to relieve the acute civilian shortage. A considerable output was planned and in full swing it should do much to relieve the position in the country. It would, however, be some time before that result was achieved, as the Government had earmarked the first 15,000 for railway use, and after this order has been executed the factory will have to carry out a number of urgent orders for military camps and hospitals in South Africa. In spite of this priority on official orders this factory has been able from time to time to place on the civilian market in the Union moderate quantities of plastic cups, saucers and plates. Production is too often held up, however, by a shortage of the essential raw materials, which come from overseas. It is hoped that further shipments of these materials will be received.

Presses for plastics are now under construction at the workshops of a Pretoria engineering firm, which is also constructing plastic machines of the injector type.

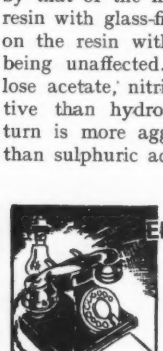
A Durban firm is also making electrical fittings in phenolics. These plugs and sockets are being made in 5-amp. and 15-amp. three-pin sizes in accordance with British Standard specifications. So far this firm has installed pilot tools for test runs on the 5-amp. size and will shortly be producing limited quantities. They are now busy on the tooling for mass production of the 5-amp. size, which will be followed by the 15-amp. size. The 30-amp. and 60-amp. fuse parts are already well in production. Impregnated plywood is now being made in South Africa by a Port Elizabeth firm.

Some other new developments in the local manufacture of plastics are envisaged and if they come to fruition local plastics will be produced in increasing quantities for a number of new uses. Actually there are an unlimited number of uses to which South African-made plastics could be put, and in spite of the possibilities of the big export markets in the neighbouring countries, it still seems that there will have to be a big reorganization of the industry before it will be on a footing to compete with the British and American plastics industries after the war. Before the outbreak of war an increasing number of British plastics were being imported into South Africa, and although this source of supply has now been cut off temporarily there is nothing as yet in the development of the South African plastics industry to suggest that the Union market will be lost to the British exporter after the war. It is being suggested in the local industry that it is essential to the future of plastics in the Union that the raw material be produced locally from available local resources, but it does not as yet seem that there is any likelihood of that happening, as it would be far too big an undertaking in the present state of South African industry. Thus it means that the South African plastics industry consists only of a few factories producing various plastic articles from imported raw material.

World's Industry Employs Plastics

CHEMICAL

Chemical resistance of plastics forms the subject of investigations reviewed by Delmonte in A.S.T.M. Bulletin, December, 1942, p.11 (abstracted in "Mechanical World," 1942/114/8). In the case of phenolic resins, effect of acid or alkali is determined not only by the nature of the resin itself, but also by that of the filler. Thus a phenolic resin with glass-fibre filler showed attack on the resin with nitric acid, the glass being unaffected. In the case of cellulose acetate, nitric acid is more destructive than hydrochloric acid, which in turn is more aggresive to this material than sulphuric acid.



ELECTRICAL

Impregnating media for cable covering and general insulation was once based principally on nitrocellulose; acetate plastics and, for special purposes, other synthetics are now available. Litzler, of the Industrial Oven Engineering Co., Cleveland, Ohio, describes treatment of cables and insulated wires with these materials and discusses the equipment necessary ("Wire and Wire Products," 1943/18/283). **"Cellophane"** has been shown to possess the highest permeability to X-rays of all the plastics, being inferior in this respect only to pure beryllium. **Multiple terminal block** of new type has been introduced by Curtiss Development and Manufacturing Co., Chicago. Particularly designed for high frequency circuits and other exacting equipment, the block consists of individual feed through terminals mounted in bakelite. These are permanently held in a metal strip in any combination desired. Terminals have ample clearance and leakage distance for circuits carrying up to 300 volts with currents up to 20 amps. The blocks are available with any number of terminal units between 1 and 10; larger numbers can be fitted if desired. **Protecting cover for dial** of megger formerly consisting of pressed metal attached to case of instrument by separate metal hinge is now moulded in cellulose acetate butyrate. Frame of cover has two side lugs which are snapped into position, their appropriate eyes embodied in the framework. Expensive hinge assembly is thus dispensed with and valuable metal saved.

GENERAL ENGINEERING

Thermal conductivity of various heat insulating materials, such as cork of different grades and grain-sizes, slag wool, glass wool, cellular rubber and ebonite and cellulose plastics, are reported upon comprehensively by Griffiths and Hickman in "Chemical World," 1942/114/16. **Thickness gauge and shim stock** of predetermined thickness is now available in a plastic material, the colour identifying the thickness. This development originated as the result of the production of spacing washers for milling cutters in a transparent coloured plastic material. **"Hard**

steel" metal for drilling hardened steels is recommended for drilling plastics. The drill used is of a triangular section with a chip clearance groove at the point. Very high drilling speeds are employed and the heat generated is, by virtue of the shape of the drill, said to be dissipated rapidly, hence no heating up of the point occurs and seizing is eliminated. It is to be noted that the drill shape for plastics differs from that recommended for steel. **Wound-tape plastic bearings** for high specific pressures form the subject of study by Gilbert and Lurenbaum, reproduced in "Automotive and Aviation Industries," April 1, 1943, page 45. **Drill jig of cast Durez resin** is used in the production of an aerial delivery container for the Curtiss Caravan, the container itself being made of hardwood veneer bonded with Durez phenolic resin adhesive. The cast jig was made directly on one of the containers, thus assuring a perfect contour. The resin, which is easily machined, has an impact strength of 0.11-0.15 ft. lb., and a compressive strength exceeding 8 tons per sq. in. Bend strength varies from 3-4 tons. Shrinkage after two hours' curing at 140 degrees F. is 0.003 in. Bushings for locating pins in the jig were inserted and fastened by the use of a low-melting-point alloy which expands at solidification. **Porous casting reclamation by means of synthetic resin treatment** is discussed by Jones in "Technical Bulletin Inst. of Prod. Engineers," April, 1943, p. 2. **Plastic housings** are embodied in a new type electric drill manufactured by the Independent Pneumatic Tool Co., Chicago, which company describes its product as being "armoured in plastic." The plastic housings of the new ¼-in. drill do not support any of the operating parts of the mechanism, but serve simply as a protective shell, rotating parts being supported within a metal skeleton to ensure their alignment. The field case, gear case, and grip handle are made of Thorite plastic and slide into position over the metal skeleton. ("Automotive and Aviation Industries," April 1, 1943, page 64.) **Plastic housing for drills** of ¼-in. and ⅜-in. capacities have also been developed by Black and Decker. The plastic used has a shredded, cotton-duck base of high impact resistance which enables it to withstand considerable abuse and wear. In this case, steel inserts are embodied in the housing to carry ball bearings, whilst steel inserts are used in the field housing for assembly screws. **Plastic handles** coloured black, green, yellow or blue to designate tolerances are used for the glass gauges being manufactured by the Langlois Gauge Co., Detroit. The gauges are ground from special glass by means of diamond powder; their cost is slightly higher than those in steel, over which they have the advantage of virtually permanent dimensional stability, and the property of being either undamageable, or, if damaged at all, only in such a way as to be very clearly visible.

MOTORS

Tyre valve cap in plastic is said to seat perfectly and hold air up to 400 lb./sq. in. without need of washers. An unthreaded "finder skirt" acts as a guide when applying the cap to awkwardly placed valve stems and a wide knurled band affords a firm gripping surface for tightening.

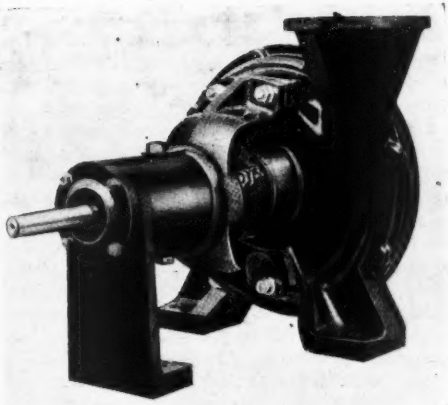
AIRCRAFT

Compound for cleaning the "organic"-glass nose sections of modern aircraft has been developed by Turco Products, Inc., Los Angeles, California. The compound is stated to be non-toxic, harmless to paint, to have no effect on the hands, to be free-rinsing and to leave the plastic surface clear and free of

any greasy film which might collect dust. **Wire baskets** in which Rolls-Royce Merlin aircraft engine parts (now being produced in U.S.A. by the Packard Motor Co.) are transported are degreased and coated with "Resistoflex" solution to avoid damaging the fine finish of the parts; synthetic resin is unaffected by the solvents used in degreasing.

MISCELLANEOUS

Plastics and laminates, hard rubber, ivory and hardwood are economically finish-machined to special forms by the use of shaped diamond tools, according to Slawson, writing in the "American Mineralogist," 1943/28/141. **Plastic moulding machinery** in U.S.A. has now been made the subject of a new allocation order in order to ensure its availability for priority purposes and to prevent needless manufacture of new plant ("Wire and Wire Products," 1943/18/291). **Shellac** forms the subject matter of a pamphlet recently issued by the London Shellac Research Bureau. This publication, presenting abstracts on shellac literature covering the year 1942, contains some 40 valuable references to articles and patents made public during that time. A consolidated subject and author index on shellac for the period of 1928/1940 is also available. **Extruded cellulose acetate-butyrate seamless tubing** is now being produced in sizes up to 2 ins. outside diameter by Extruded Plastics Inc., Norwalk, U.S.A. An extension of the range of 2½ ins. diameter is contemplated to meet war-time requirements ("Machine Design," May, 1943). **Self-ignition temperature of cellulose** was determined at the National Bureau of Standards, U.S.A. In a highly pure form, as filter paper, ignition occurred at 232 degrees C., after seven-nine hours of heating; at 246 degrees C., ignition occurred after three hours' heating; at 253 degrees C., after two hours of heating and at 280 degrees C., after half-hour heating. Forty-five hours at 230 degrees C. and 70 hours at 228 degrees C. did not result in ignition. The lowest self-ignition temperature of cellulose in the form of cotton wool was 266 degrees C., after 2½ hours, no ignition resulting on heating at 263 degrees for eight hours, or 264 degrees C. for 17 hours. The weight of carbon residue resulting from these tests was determined. For comparative purposes **self-ignition temperatures for magnesium** were also determined. Cut ribbon ignited at 540 degrees C., 30-50 mesh powder at 510 degrees C., 50-70 mesh powder at 508 degrees C., 70-100 mesh powder at 504 degrees C., 200-325 mesh powder at 492 degrees C., and 325 mesh powder at 473 degrees C. Magnesium containing 1 per cent. aluminium and 1 per cent. other additional elements gave values approaching these to within 10-15 degrees C. ("Technical News Bulletin," October, 1942). **A polymer-plastic base** is used in a new emulsion, designed for rendering the surface of various metals photo-sensitive, manufactured by Le Roys Research Laboratories, Elizabeth, N.J. The new emulsion dispenses with gelatine, hence it is not susceptible to deterioration in storage. **Induction heating of moulds** results in greatly increased possibilities of high output rates, according to Meharg (Bakelite Corp.), writing in "Machine Design," July, 1943, p. 103. The author presents numerous curves to substantiate results of investigations. Included amongst the curves are those for optimum moulding times for various sections, together with curves of pressure for moulding as a function of moulding time. **Engineering aspects of plywood** are dealt with in the same journal (p. 115) by Peterson, Aeronautical Engineer, Civil Aeronautics Administration. Particular attention is called to the curves presented by the author demonstrating allowable stresses and permissible sheer stress concentration effects in wooden members are also considered.



Centrifugal pump for handling mineral acids. This apparatus may be constructed in a phenolic resin or in suitable grades of polyvinyl chloride. In a succeeding illustration the component parts of the pump are shown.

Plastics for Chemical Plant

A Report from "Materie Plastiche," 1942/11/26, on an Italo-German Autarchy Convention Convened in Turin in November, 1942

By G. LOMBARDO (Soc. Montecatini)

IN the past, the choice of means for the industrial preparation of a certain product lay amongst those which research in the laboratory had brought into use, and had to be one which the available apparatus would allow of, even if that meant falling short of the best results.

Now, however, in order to obtain the best results, a more favourable issue and lower prices, every difficulty is faced and practically always overcome.

All this is possible because chemical apparatus has undergone vast improvements, which make it possible to reach pressures so high as at one time to be considered prohibitive, to weigh accurately according to the stoichemetric proportions of the component parts, to reach and maintain high or low temperatures much more accurately, and to produce more efficient and more selectively sensitive catalysts to bring about new reactions.

So one by one problems arise to solve which it requires not only the continual elaboration of available means in their most suitable form but also the careful choice of materials which will best respond to the case in hand, so as to get the best out of the plant, without endangering the life of the plant itself.

Continual study has, of course, been necessary in order to evolve apparatus which will allow of such exceptional working conditions. This study has been drawn from the practical observation of the different elements which form apparatus made of materials of different nature and behaviour.

It is actually in the search for these new materials, materials which had to give the designer those greater possibilities required by the conditions of work referred to above, that plastics, or rather certain types of plastics endowed with special characteristics, have been so specifically applied. Their use has been marked by continual progress, because these materials, when reasonably employed, have lent themselves most advantageously to the improvement of chemical apparatus, whether as regards

the results of more complex working demands or the longer life of the apparatus itself.

Among the characteristic qualities of those plastics suitable for the work in question, the most interesting are as follow:—

(a) Resistance to chemical corrosion.

(b) Absence of phenomena of electro-chemical corrosion.

(c) Heat-resisting properties.

(d) Low specific gravity.

(e) Structural behaviour of the plastic components.

In the past no materials existed which united such qualities, which have opened up new possibilities to the designer.

Types of Chemical Plant

In order to illustrate more clearly the position held by plastics in the field of materials at present at the disposal of industry for the construction of chemical plant, it is as well to consider the process of evolution which has marked chemical plant. Most especially might we consider that field of available material pertaining to the handling of liquids.

The important processes of synthesis and transformation characteristic of modern chemical industry involve the movement of large masses of liquids. This is also the case in numerous other activitives more or less connected with chemical industry.

A circulating system for fluids consists essentially of an assemblage of pipes, joints, fittings, valves, tanks and pumps. The last of these, constituting the propelling force, are of fundamental importance to the working of the whole system, and were, therefore, and still are, the most carefully studied by engineers. Piston-type pumps, rotary pumps, valveless pumps, screw pumps, and gear pumps are examples of very different types which have been worked on specially for chemical industry and which, in course of time, have undergone such an evolution that some have been surpassed and have gone out of use, whilst others have still further strengthened their position.

From the point of view of the effect which the liquid under examination may have on the different parts of a pump, a distinction can be made between those pumps in which the liquid does not come into contact with the working parts and those pumps in which such contact does take place. To the first group belong piston pumps of a special kind; in these the working face of the piston is separated from the working space by means of membranes or liquids, or by some other intermediary means performing a protective function. To the second group belong the other kinds of piston pumps and centrifugal pumps.

The rotary movement peculiar to centrifugal pumps allows of great simplicity of control, with no need for complicated transmission system.

When applying centrifugal pumps of a normal type to the handling of corrosive liquids, the first measure taken was to remove the bearings which support the shaft from the range of corrosive action by the liquid.

That, of course, led to a considerable increase in the vibration of the wheel and necessitated a different design of the whole casing so as to prevent harmful vibrations. Next to be considered was the problem of the packings of the stuffing box.

Evolution of Diaphragm Pump

The life of the packing is shortened both by the chemical action of the corrosive liquid and by the mechanical wear due to the friction of the packing rings on the shaft. It is shortened also by the high temperature caused through the heat of the friction, which can increase the corrosive effect of the liquid. Finally, it is shortened by the phenomena of cavitation, which generally have similar effects to those already mentioned.

It was, therefore, decided to do away with the stuffing rings, and there arose the so-called pump without a stuffing box. In this the necessary liquid-tightness is secured by two opposed circular rings of metal, which when the pump is stationary press one upon the other, and when in movement are held far enough

apart to prevent friction by an axial component of the centrifugal force, to which all masses attached to the rotating shaft of the pump are subjected.

The joining of the impeller to the shaft has been studied with the view of facilitating the changing of those parts which bear the greatest strain and which, therefore, have the shortest life. Packing discs and labyrinth passages prevent any possible escape of liquid or vapour from penetrating to the mechanical part of the pump which they might damage.

The valves have also gradually undergone development in design until the free-flow type has come into use. The internal shape of these valves is such as to cause the least deviations in the free flow of the liquid, and thus largely eliminates those turbulences which nearly always give rise to deposits and incrustations, causing the valve itself to deteriorate and its hydrodynamic efficiency to decrease.

Another precaution taken with the valves against corrosive liquids is to remove to the exterior the threaded part of the valve rod in order to prevent incrustations from hindering its movement. These valves are, therefore, provided with a valve rod bridge, through which the valve rod is screwed. The seating of the stuffing box is so built as to allow of an easy change when the phenomenon of corrosion proceeds to a greater extent than is permissible. The member which effects closure is usually of an elastic nature—that is to say, a stopper with an elastic coating, which is able to adapt itself to any roughness on the surface surrounding the part.

Selecting Materials of Construction

Turning to consider the materials generally used, let us note that the simplest conditions are those when it is possible to use exactly the same materials as would be suitable for the handling of pure water. In such a case there is a wide choice amongst those materials already well known and established, and which will allow of modifications required to satisfy operating conditions.

Quite another problem arises when the choice of material and the principles upon which the design is based are subordinate to the necessity of facing the very special conditions enforced by the handling of corrosive liquids. Alloys of iron and silicon, or chromium, and nickel, bronze, aluminium and its alloys, hard lead, plain cast iron either rubber-coated or enamelled, stoneware, and so forth are among the best-known materials, and their possibilities for use with different corrosives have already been clearly established both in the experimental and the technical field. Thus in choosing them one can be guided by practical experience and knowledge of the mechanical characteristics peculiar to each material.

Comparing Plastics and Metals

There is actually a most impressive collection of materials ready for use, which in their different categories and in their numerous types present the widest range of physico-chemical characteristics. This very range, whilst satisfying the most diverse needs, demands by reason of its size, the most careful selection; and this is done to achieve the best results from the material selected, both from the point of view of its properties as well as the operating conditions.

With such considerations in mind, it would be useful to glance at a few special examples which will illustrate one of the many cases laid before the engineer in the choice of material most suitable for his needs. These examples will at the same time help to confirm those conclusions which can be drawn from a technical and economic comparison between material of what we might call traditional usage, and plastic materials which in this field are the most recent contribution of science.

With this intention in view let us consider the case of alloy steel capable of resisting corrosion by aggressive chemical agents.

Such types of steel can be roughly divided into two classes: temper-hardening chromium steels of various composi-

tions which have a martensitic structure after tempering, and a pearlitic structure in the annealed state, as well as the temper-hardening ferritic varieties, and the nickel-chromium alloy steels which cannot be hardened by tempering and which have an austenitic structure. Side by side with these two main classes there are all the modified compositions which have been evolved by practical experience and which represent the more or less comprehensive solutions of as many special problems.

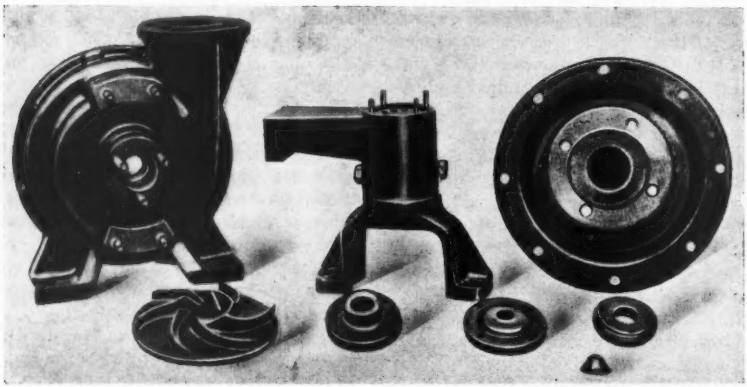
Although all these kinds of steel enter as a whole into the class of stainless steels, since, strictly speaking, each of these possesses such properties to a greater or lesser degree, the types which are generally included in this classification are the nickel-chromium steels. In the years immediately preceding the present conflict they acquired wide renown in the whole field of industry, and particularly the chemical industry. Their use has spread to such an extent as to cause in not a few cases a real abuse, in the sense that their use is not always justified by real technical needs.

Stainless steel—considered as a typical example of a corrosive-resistant material —does not, however, provide a complete solution to the problems encountered when constructing chemical plant. It is not the ideal material for general use, and on the contrary in not a few cases it has been found deficient.

If we consider the types most generally used, represented mostly by steel with a content of 18 per cent. chromium and 8 per cent. nickel, we can form a conception of the real possibilities of such materials in contact with those corrosive liquids most commonly encountered in normal industrial work.

In the case of concentrated sulphuric acid, it is necesary to limit the temperature when using stainless steel, for at high temperatures corrosion becomes equal to or greater than 10g/m²/hour. Such limitations, although they are not encountered with considerably less highly concentrated acids, are still a sign of deficiency in the material when in contact with the acid, which, considering its vital importance, may be called "the king of acids."

Nitric acid has a no less harmful action, and in the highest or medium concentrations results in an attack which, it must be admitted, very few materials can withstand. Among the halogen acids, notoriously highly corrosive,



Detailed view of component parts of the acid pump shown in the illustration at the head of this account. Note particularly the adaptation of design to suit the working properties and mechanical characteristics of plastic as contrasted with metallic materials.

hydrochloric acid in the anhydrous state can be satisfactorily handled in stainless steel of the above composition, whilst quite another situation arises when the gas is moist, or in the case of the highly concentrated acid; in the latter case the material behaves in a manner only slightly better than it does with hydrofluoric acid, which will attack any kind of steel, and causes corrosion of an exceptionally high degree, certainly higher than the limit of 10g/m²/hour. Fluosilicic acid has almost the same effect.

Case of Organic Acids

The less corrosive nature of organic acids naturally gives them a more favourable position as regards the use of stainless steel, which generally behaves very well when brought into contact with them, although in quite a few cases even with these compounds a careful estimate is needed of the most appropriate type of steel. With regard to this it is as well to remember the highly corrosive action of hot acetic acid, which steel of the 18/8 type, especially at welds, will not completely resist.

The reference to stainless steel is not meant to exclude the possibility of using other metals, e.g., iron, copper, aluminium, magnesium and alloys in chemical plant.

But since all these materials permit an even more limited use than stainless steel, it would be useless, given the purpose of the present paper, to enter into a detailed discussion of their reactions to corrosive agents.

Besides metals mention may be made of certain materials of the stoneware type which, however, side by side with the undoubtedly valuable attribute of resistance to nearly all corrosive liquids, except hydrofluoric acid, show such a lack of mechanical resistance as to make it unwise to use them for various purposes.

To considerations of a technical order may also be added arguments of an economic nature, all the greater at the present moment seeing that the materials mentioned either come under the category of imported goods, or are largely turned to uses of a war-like nature, or require for their production materials obtained chiefly abroad.

Thus the use of stainless steel, already uneconomical in itself because of the intrinsic cost of the alloy elements and the natural difficulties of working, has considerably diminished owing to the lack of certain constituents, especially nickel. As a result of this there has been recourse to the method of cladding with sheets of stainless steel, to the use of chromium-alloy steels, the applicability of which is naturally more restricted, and finally to types of chromium manganese steels. These last, although of an austenitic structure similar to that of the chromium-nickel steels, are less resistant to intercrystalline corrosion.

Quite recently the grain size of these steels has been refined by the introduction of nitrogen into the mother metal and this has resulted in improved welding properties and better corrosion resistance.

Combinations of Various Materials

In a production process it does, in fact, often happen that the nature of the materials chosen for the conveying apparatus is not the same as that of the reaction vessels themselves. This involves the need for large reserves of material assorted according to quality.

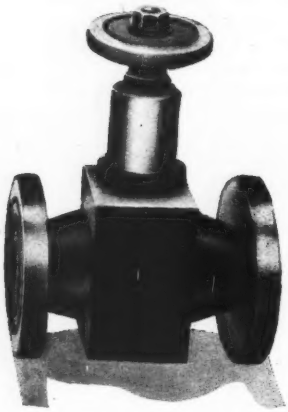
Putting aside the economical situation, which is of an uncertain nature, it does at any rate appear clearly that the field for applying the materials so far most commonly used is generally limited.

Chemists must therefore continue with their counter-measures creating on the one hand new materials able to resist any rapid corrosion. On the other hand engineers must perfect the design of every piece of apparatus so that the parts most subject to attack should be those best able to resist or those most easily replaced.

Of these two methods which will be able to bring us to the solution of such an important problem, the first has allowed us much headway thanks to the production of certain kinds of plastic bodies made of home-produced

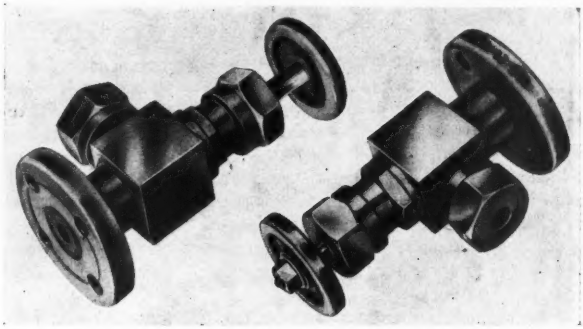
materials with specially marked anti-corrosive qualities, and it will be possible to make further headway with the new plastic bases which one by one pass from the laboratories to practical use.

The plastics particularly concerned are the thermosetting phenolic materials with



latter type, and particularly polyvinyl chloride, possess excellent anti-corrosive qualities and offer wider possibilities, inasmuch as they resist even the corrosive liquids which the phenolic resins, already mentioned, cannot resist. The only exceptions are certain organic solvents for which, however, the above-mentioned phenolic materials can be used with excellent results.

The contribution of these materials to the solution of the problem of corrosion appears clearly if we remember the inconveniences already stressed before with reference to the limited scale of corrosive chemicals which all the better established materials mentioned, metal and non-metal, can resist. Moreover, such special types of plastic materials can at the same time resist a very large number of corrosive chemicals, whilst they are not subject to corrosion of an electro-chemical nature. What is more, their resistance is practically identical all over, whereas, as shown before, other materials can have areas which, when



Pictured above is an early type of valve in polyvinyl chloride produced by machining from the massive material. At the right are more recent valves built up from smaller components machined from rod stock.

mineral fillers and thermoplastic materials such as polyvinyl and polystyrene resins. The former are indeed unaffected by all the corrosives generally used in industry, to be more exact, by organic and inorganic acids even highly concentrated, with the exception of very strong oxidizing acids such as chromic and nitric acids, and also the caustic alkalis. Such materials behave satisfactorily up to temperatures of about 150 degrees C. The they are altered by requirements of fabrication (hardening, welding and so forth) are subject to increased attack in a measure fatal to the life of the whole plant.

To the advantages of an economic order achieved as the result of quantitative replacement of scarce metals must be added advantages of a technical order resulting from the greater chemical resistance of apparatus built with plastic,

not to mention the more satisfactory performance of the plant and the purity of the liquids handled.

It is not possible at the moment to give precise documentary evidence complete with factual data in support of these exact results which have confirmed what had been already foreseen, but a few examples may be quoted.

A few centrifugal pumps of a special phenolic material which have been working continuously for more than two years handling 27 per cent. acetic acid containing 1 per cent. sulphuric acid and at a temperature higher than 100 degrees, to-day appear in perfect condition and give every assurance of being able to continue their work for many years.

Another interesting case is that of pumps, also of a special phenolic material, employed for over a year in handling fluosilicic acid in concentrations varying from 10 to 15 Bé.

The interiors of these pumps are absolutely perfect and give promise of remaining completely efficient for an indefinite length of time. As is well known, no type of stainless steel offers adequate resistance to fluosilicic acid.

Resistance to Ethylene Chlorhydrin

Lastly may be quoted the example of receiving containers also of a special phenolic material, which in contact with ethylene chlorhydrin have shown no trace of chemical change, contrary to what happens in practice with any other material of general use.

Having specified the advantages which plastics could offer when used in the construction of chemical plant, chemical engineers assumed the task of proceeding to the gradual substitution of metals in all cases where such a change would lead to the advantages already described.

Naturally a systematical study has been necessary to arrive at designs most suitable for each particular case which has to be dealt with, since obviously pure and simple reproduction was not possible.

Clear indications of all this work of adapting are to be found in the evolution which the principal pieces of plant for chemical industry have undergone in the course of time. From this point of view it would be interesting to give a brief analysis of a few of these types of plant.

We may begin with the centrifugal pumps, which are the most widely used for handling liquids in chemical works. They probably suffer the most, because the simple chemical attack is aggravated by phenomena of cavitation inside the pumps, and by the mechanical action of the liquid, which, flowing over the walls of the pump, carries away any surface protective compounds produced by the corrosive attack; this action exposes successive layers to the corrosive action. Finally, the liquid wears away the surfaces with which it comes into contact because of the abrasive action of the solid impurities which it contains to a greater or lesser degree.

Details of Pump Design

The volute of pumps made of plastic materials is essentially of the same design as that of types made of costly metal, except for a few details introduced to help the moulding of the volute by means of the well-known procedure of pressure moulding in a steel die in a hydraulic press. The connection between the various parts is assured by stainless steel bolts which are moulded into the plastic parts.

The impeller is of the open type to avoid unnecessarily complicated moulds, and thus avoid difficult moulding which impellers of the closed type would require without the reward of adequate advantages.

Continual perfecting has been necessary for the mechanical part, to avoid deformations of a permanent nature produced in the parts made of plastics, which had to support the moving metal parts absorbing the inevitable vibrations to which they are subject.

The problem of the stuffing box, already so serious for centrifugal metal pumps, has been even more complicated in the case of pumps in plastic material.

Indeed, working conditions for pumps of plastic materials are worse, since the

heat which develops in the stuffing box cannot pass through to the outside because of the low thermal conductivity of the structural material. The temperature tends to rise considerably. Such a temperature is positively prohibitive for thermoplastic materials (e.g., polyvinyl and polystyrol compound) and for these products certain arrangements have been made which consist in introducing a protective metal sheet between the rings of the stuffing box and the plastic interior.

The results obtained are, however, only mediocre, and for thermoplastic materials it is considered necessary to use the types of pump without a stuffing box. In this case also, however, the same design which has been adopted for metal pumps cannot be employed since the heat caused by the friction on the surface of the packing might be harmful to the materials nearest the surface.

Thus special methods have to be employed and amongst them we note an arrangement which by making use of the inertia of certain parts causes the removal of the surfaces of the packing before the pump is actually set in motion and also causes the closing of the pump when it is being stopped, thus eliminating friction between the surfaces of the packing and consequently the development of heat.

Production Methods

For constructing valves in plastics recourse to pressure moulding is necessary; for thermoplastic materials machining is frequently used, as in the case of metal valves but starting from a moulded setting off blank. Other methods include the welding together of machined parts or parts obtained by extrusion.

Generally speaking, the most preferable and economical method is not pressure moulding which, in the case of thermoplastic materials and particularly of polyvinyl chloride, is a very delicate task, since it requires an absolutely constant uniform temperature and a skilled handling of the thermal balance which depends on the heat capacity of the die.

Fortunately, valves of the free-flow type which are most advisable for corrosive liquids are also the most suitable design for production by means of injection moulding since they allow the cones which form the internal cavities to be easily withdrawn.

Valves in plastic materials do not, therefore involve great differences in design except for the presence of ribs which strengthen the connecting flanges, and except for the method of fixing the plug seating where a shrink fit cannot, of course, be used, but which is glued into position by means of a resin-base adhesive.

Pipe-joining Systems

For pipes it is worth pointing out methods of joining, amongst which we may draw particular attention to the one we consider most suitable, that is to say, joining by means of loose flanges which rest on sleeves either welded or screwed to the pipes.

For other plant, like reaction vats, various tanks, etc., there are no details worth noting concerning the lining of these vessels with sheets of polyvinyl chloride which are generally held in place by means of an adhesive made up on the basis of the same resin.

In conclusion, it is hoped that the aim of this paper has been reached, that is to call the chemical engineers' attention to plastics in order that they may realize their ever-growing importance, and acquire a wider knowledge of them, and in order, too, that they may make use of them in their designs, either to overcome any possible difficulties, or to obtain that perfecting of the plant itself which plastics allows if used with the necessary skill.

The particular applications given as examples of the use of certain types of plastics is certainly very expressive, but it does not in the least mean that the chemical resistance possessed by these materials constitutes their principal characteristic. On the contrary, other very important properties, such as their heat-insulating properties, their dielectric properties, special methods of fabrication,

low specific weight, and others make them suitable for equally interesting uses in other sections of industry.

Future prospects are therefore extraordinarily bright, but what gives us particular pleasure is the greater value assumed by results already reached when related to present needs. But even if we do not wish to draw a more general picture of the value of plastics in the field of chemical industry alone, this value is of note if we remember the part played by chemical industry in war-time economy.

It will be sufficient to remember that explosives, pharmaceutical products, fertilizers, different metals, chemical products for industrial purposes, etc., are derived from processes belonging to chemical industry. So I do not think it would be exaggerating to affirm that it would be impossible to re-order our war economy if we renounced even one of the means which chemistry has given us. That is why to-day more than ever it is absolutely essential that chemical industry should be in a position to draw from its own apparatus the highest productive effort, conquering all obstacles which might lessen output.

Plastics and War Effort

The contribution of plastics is therefore of exceptional importance, because it has been possible to substitute these products for other materials which are increasingly difficult to obtain, such as rubber, vulcanite, copper, lead, bronze and tin, allowing the building of new plant and the maintenance of that already working, which if attacked by corrosion might have been put completely out of use.

As well as contributing so successfully towards assuring chemical industry the means of carrying on regularly and indeed of increasing its activity, plastics have allowed large quantities of valuable metals and other material for which they have been substituted to be turned to other uses of urgent need.

Many special machine tools, very valuable and scarce, have been released, and parts have been produced by the moulding technique which before had to be made by machining. All this is derived from plastics, and it really is a pity that our great need for haste does not allow of a moment's pause to take a census and show with the eloquence of figures the impressive value of the contribution that plastics have made.

What has been done, however, is not the finishing but the starting point for new successes.

Whilst other more ambitious works are being studied, our laboratories are fashioning more plastic materials with increasingly valuable properties which will allow us to proceed beyond the stage already reached with the plastics to-day at our disposal.

The Future Assured

The future is certain, because the advantages obtained compared with the materials traditionally used for the same purpose are so remarkable that the use of plastics is already definitely established.

This emerges very clearly from the examples treated in this survey. But also in the great majority of their other uses, plastics have allowed real advances in the evolution of every design.

The valuable substitution which they have made possible has not marked out these products being only emergency materials, and so we can count on their help when normal conditions return and when once more all the productive energy of the new Europe will be mobilized for social progress.

It should have been made quite clear in the foregoing discussion that plastics, no matter of what type, are in no way to be considered as substitutes, using this word in the customary somewhat derogatory sense. True, indeed, they are "replacement" materials, ousting in many instances the older and more traditional media solely by reason of more specialized physical, chemical or mechanical characteristics, and partly for economic reasons. Above all, however, plastics are, in essence, specialized materials for specialized purposes.

Metallizing Plastics
(continued)

A Complete Survey and Critical Study of the Modern Methods of Metal Film Formation on Plastics for their Protection and Decoration

by E. E. HALLS

3. Metal Coatings Applied from Metal Wire, Powder or Liquid Using " Hot Pistols "

(Contd. from August issue, p. 348)

The corrosion resistivity of sprayed metal coatings is closely the same as that of the metals concerned except in so far as the roughness of the surface may exert a secondary influence in specific cases. When much handling is entailed, as through numerous assembly and inspection operations, " finger-marking " is prone to occur, and as a result some localized staining, discoloration or corrosion may result. Generally, depreciation in appearance is the only concern. When or where electrical contact is not involved the finish can usefully be lacquered or varnished. The good key provided by the rough surface for adhesion enables clear colourless cellulose lacquers to be employed for the purpose, and they adequately fill the role providing a suitable thickness is applied. A medium high consistency lacquer fulfils most requirements. Characteristics of such lacquers are given in Table 16. These can be thinned to spraying consistency with thinners No. 1 shown in Table 22.

Table 16.—Laboratory Characteristics of Clear Colourless Cellulose Lacquers.

	No. 1	No. 2
Compositional:		
Volatile spirit (loss in wt. 3 hrs. at 110°C.) %	86.5	87.0
Total solids %	13.5	13.0
	100.0	100.0
Ash on incineration %	0.03	Traces
Physical:		
Specific gravity at 25°C. ..	0.885	0.886
Viscosity at 25°C. in centipoises	1,020	2,000

For both materials, dilute with thinners to a viscosity of 250 to 300 cps. for spraying.

Again, sometimes the metal-sprayed plastic work has to be used under open weather conditions or in other severely corrosive atmospheres. For very severe exposures, such as continuous operation in open weather, finishes using synthetic resin solutions can be chosen. Where it is important to prevent oxidation of the surface of the metal coating, the type of phenolic resin finish described in " Plastics," November, 1941, under the title of " Weatherproofing Cellulose Acetate," is admirable. It has proved successful in preserving zinc-sprayed coatings for all-weather exposure. Other protective finishes can be used, of course, including the spar varnishes of china wood oil base, air-drying or stoving synthetic varnishes or lacquers, particularly of the alkyd, oil-modified alkyd or urea-alkyd resin varieties, and cellulose lacquers. Pigmented finishes can be used when desired for opacity or colour reasons.

In connection with the use of zinc-sprayed bakelite paper or fabric laminated sheet under open atmospheric conditions, a number of tests have been carried out on samples.

Table 17 gives the results of these tests on a specimen of 1/64-in. thick bakelite laminated fabric sheet, zinc sprayed by the powdered metal process. It will be noted that the metal coating was relatively thin for a metal-sprayed layer, but its adhesion, as shown by scratch tests or by fracture, was exceedingly good. Under the various exposure tests to which applied, very little damage to the zinc

Table 17.—Exposure Test Results on Metal Sprayed Phenolic Laminated Sheet.

Test panel comprised phenolic fabric laminated sheet, 1/64 in. thick, zinc metal sprayed 0.001 in. thick (powder method).

Test No.	Test conditions	Behaviour of specimen
1	Wet heat, 2 cycles to Spec. WT.K.110	General slight whitening of the zinc coating during first cycle. No further change on second cycle. Adhesion not impaired
2	Salt spray exposure at normal temperatures	General whitening of the zinc coating developed from the first day. This tended to form a protective coating and in two months no other deterioration was apparent. Adhesion of the zinc coating was not impaired
3	Humidity test, hot day, cold night	In three months, general slight whitening, but virtually no deterioration. Adhesion of the zinc coating was not impaired

Measured thickness of zinc coating, average :—
Expressed in terms of milligrams per square inch 90
Expressed in terms of linear thickness.. .. .. .. 0.0015 in.

coating occurred, deterioration mainly consisting of surface oxidation, this surface oxidation probably helping to fill the pores and to protect the main layer. It is important to note that adhesion was unaffected.

In Fig. 9 the zinc-sprayed specimen used for the salt spray test in Table 17 is photographically recorded to show the condition of it at the end of two months' exposure.

In Table 18 a somewhat similar series of test results are given for a specimen of ⅛-in. thick phenolic laminated paper sheet zinc metal sprayed by the powder process. The metal-sprayed layer was then further protected by two coats of the phenolic synthetic resin solution, specially designed to have weatherproofing properties, referred to above. It will be seen from all the tests to which subjected that the material was virtually immune from attack and that, in particular, adhesion of the zinc to the bakelite material and of the organic finish to the zinc were not in any way impaired. The measured thicknesses of the coatings on the specimens in this case were varnish 0.0030 in., zinc 0.0020 in. (140 mgms./sq. in.) average.

Further exposure test results of interest are given in Table 19. These concern phenolic laminated paper sheet material sprayed on the same surface, half with zinc and half with copper. They are particularly interesting in that they show the

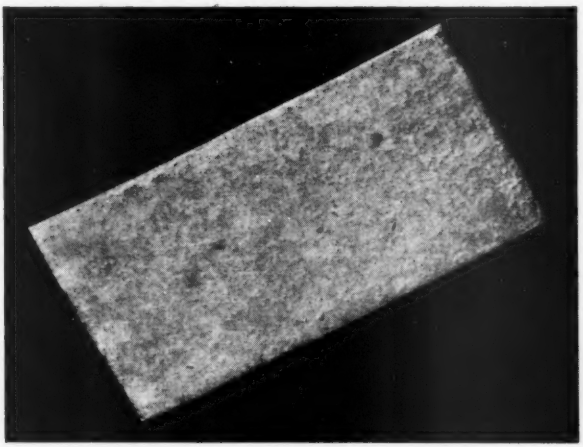


Fig. 9.—Laminated fabric sheet zinc sprayed, after six months.

Table 18.—Exposure Test Results on Metal Sprayed and Varnished Phenolic Laminated Sheet.

Test panel comprised phenolic paper laminated sheet ⅛ inch thick, zinc metal sprayed 0.001 inch thick (powder method), and varnished with two coats of air temperature polymerizing synthetic resin solution.

Test No.	Test conditions	Behaviour of specimen
1	Wet heat, 2 cycles to Spec. WT.K.110	Entirely unaffected
	Followed by salt spray exposure at normal temperatures	A few small blisters evident in two months, otherwise unchanged in three months
2	Humidity test, hot day, cold night	Entirely unaffected in three months
3	Open atmospheric test	Entirely unaffected in three months

influence of the bimetallic junction of two widely dissimilar metals, zinc being highly electropositive and copper electronegative. Under the very accelerated salt spray conditions, rapid corrosion occurred. Under the milder conditions, spoilage of appearance was the chief deterioration. Again it is stressed that adhesion was unimpaired.

For spraying the bakelite plastics, some metal sprayers apply copper over a primary coating of zinc. There is no apparent reason for this unnecessarily complicated procedure, and explanations such as improvement in adhesion or to grade the spray temperature effect have no valid foundation. First, the procedure is unnecessary, and, secondly, it serves no useful purpose. Thirdly, it is detrimental. It tends to favour poor adhesion, since stoppage between the two metal sprays is unavoidable, and this causes poorer adhesion between layers than is experienced in a built-up coat formed by uninterrupted spraying. Further, it gives the intimate bimetallic junction that accelerates deterioration.

The bimetallic effect emphasizes the need for discretion with respect to components assembled in contact with metal-sprayed coatings. Some observance of the electro-chemical characteristics of the metals must be afforded. Brass, bronze, copper and nickel-silver to copper is satisfactory, but these metals against zinc are undesirable. Aluminium and zinc-plated steel to zinc are satisfactory. However, when dissimilar junctions cannot be avoided, the joint can be sealed against the ingress of moisture by means of suitable varnish, such as a china wood oil base material or one having air temperature polymerizing bakelite resins as the basis.

The conditions for the exposure tests referred to in the tabulated data are briefly recorded below:—

K.110 Conditions.—These comprised the following cycles:—

First Cycle.—Exposure to dry heat,

Table 19.—Exposure Test Results on Metal Sprayed (Wire Process) Phenolic Laminated Sheets.

Specimens consisted of panels shot-blasted and sprayed half surface with copper and half with zinc, to give bimetallic junction. Average thickness of coating 0.005 inch.

Test No.	Test conditions	Corrosion of metal coating	Adhesion of metal coating
1	Salt-spray conditions	Bimetallic junction caused rapid corrosion, copper becoming dark and zinc white. In nine days copper mainly corroded away. In fourteen days zinc mainly destroyed	Intermediate tests for adhesion indicated no reduction in the bond to the base material
2	Humidity conditions	Gradual staining during first fourteen days, thereafter no apparent change in six months	Adhesion unimpaired, remaining excellent
3	Open atmospheric conditions	During first fourteen days, gradual staining and discoloration. Copper became whitish, copper zinc junction became dark, and zinc became whitish. At end of six months, surface dirty due to collection of atmospheric dust, but otherwise no further corrosion deterioration	Adhesion entirely unimpaired, remaining excellent

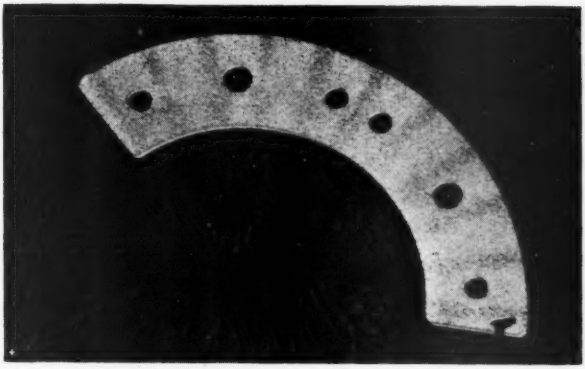


Fig. 10.—Insulator made from zinc-sprayed laminated sheet.

gradually rising in an electric oven to 71 degrees C., holding at this temperature for 6 hours, then cooling off in the oven for 16 hours.

Second Cycle.—Exposure in a uniformly controlled chamber at 60 degrees C. and 95 per cent. min. humidity for 6 hours. Cool off in the chamber for 16 hours permitting condensation upon the specimen. Remove specimen, wipe dry and leave in a circulating atmosphere at room temperature for ½ hour.

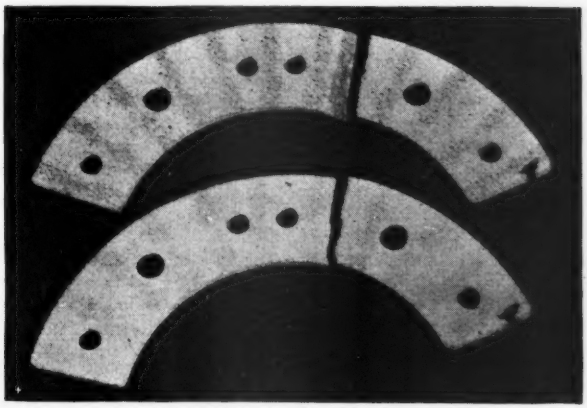
Third Cycle.—Repeat of the second cycle.

Salt Spray Exposure

Specimens were exposed to the mist produced by atomizing 20 per cent. salt solution with compressed air in a closed cabinet. The test was conducted at room temperature with the spray operating for the 8-hour day period, and the specimens left in the cabinet in the mist-laden atmosphere for the remainder of the day. Once a day they were removed, rinsed in clean cold flowing water, dried on a soft cloth and examined.

Humidity Exposure

Specimens were subjected to fluctuating conditions of temperature and humidity in a closed cabinet. A 24-hour period comprised a warm 8-hour day at 55-60 degrees C. with humidity between 65 and 75 per cent., and the night period cooling off to atmospheric temperature with humidity



Samples of the same insulators broken to show complete absence of flaking of metal.

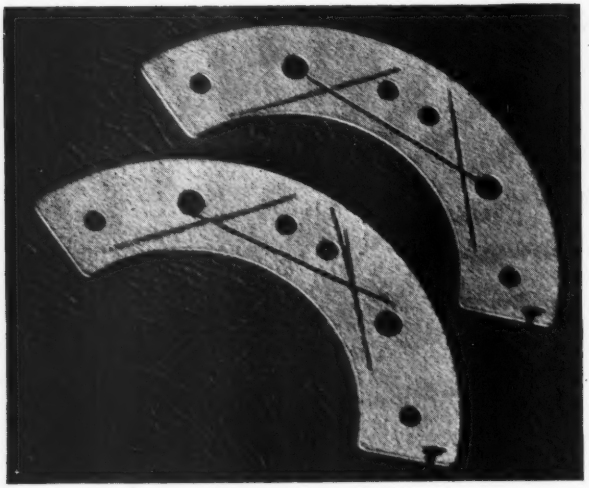


Fig. 12.—Results of scratch tests on zinc-sprayed insulators.

rising to 100 per cent. causing condensation upon the specimens. These conditions were obtained in a zinc-lined teak cabinet tightly closed with a glass cover. Temperature was obtained with electric heaters within the cabinet, controlled by means of an external rheostat. Humidity was obtained from trays of water in the base and uniformity of atmosphere was achieved by means of a fan.

Atmospheric Tests

These merely comprised exposure to the open atmosphere, the specimens being fixed to a duralumin framework facing south-west and located on a flat roof in an industrial area.

In the tabulated data it will be noted that stress has been laid upon adhesion and retention of adhesion. These qualities are considered to be very important, and it is considered that properly applied sprayed metal coatings on plastics fulfil the demands excellently. Adhesion can be judged by many forms of test, including behaviour under tension or impact stresses, but in a simple fashion it may be assessed without special equipment by means of bend and scratch tests. On bend tests, folding the coated material around a radius equal to the thickness of the material should be practicable without flaking or cracking of the spray metal coating as a result. Such a test can only be applied to flexible materials, such as cellulose acetate, and then only within limits of thickness. For less-flexible materials, in thinner sizes, the fracture and appearance of the coating upon cross-breaking can be examined. Scratch tests have no such limitations and one standard employed is as follows:—The tool employed is a hardened steel rod, tapered to the frustum of a cone, conical angle 15 degrees and diameter of frustum $\frac{1}{16}$ in. This is drawn vertically across the surface with firm hand pressure in such a manner that it just cuts through the coating to the surface of the base material. The track produced should be clear cut with no jagged edges. Two such cuts made crossing one another at an acute angle should cause no flaking of the coating from the included angle, and it should not be possible to flake the metal away from this area with the thumb nail.

Metal spray coatings upon phenolic laminated sheets of paper or fabric base withstand these tests satisfactorily, not only upon thick materials, but even on flexible sheets down to 1/64 in. in thickness. Metal-sprayed stock withstands

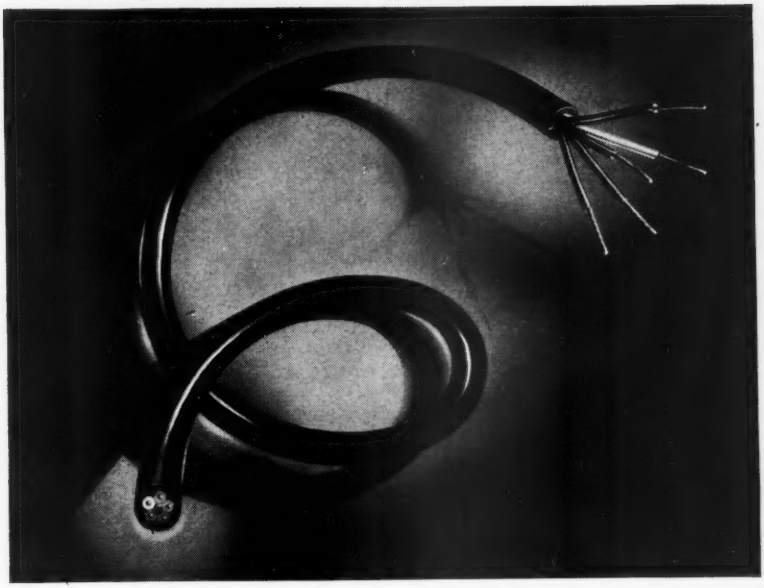


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Table 20.—Uniformity of Thin Zinc Sprayed Metal Coatings (Wire Pistol Process) on 1/32-in. Phenolic Laminated Paper Strip as shown by Thickness Measurements on Blanked Components.

Component No.	Average measured thickness, in.	Thickness, average, in terms of mgms./sq. in.
1	0.0018	79
2	0.0016	57
3	0.0016	65
4	0.0017	81
5	0.0019	87
6	0.0015	64
7	0.0019	76
8	0.0015	59
9	0.0016	56
10	0.0018	72
Mean	0.0017	70
Highest	0.0019	87
Lowest	0.0015	56

Approximate ratio of density of sprayed zinc coating to density of solid zinc = 0.37

subsequent machine operations of cutting, sawing, drilling, blanking and piercing without detriment to the coating. A notable instance where mass-produced components have been made from phenolic paper laminated of thickness of the order of 1/32 in., zinc sprayed by the wire process, concerns telephone switch banks. Here separators normally produced from aluminium strip of close dimensional tolerances have been fabricated from metallized plastic, the metallizing being essential for commoning with copper tape and electrical earthing. The material in strip form is roughened by shot blasting on both sides and then sprayed with zinc (1.5 mm. wire) both sides to a thickness of the order of 0.002 in. The data in Table 20 shows the uniformity with which this can be achieved. The components are then blanked and pierced and stored ready for assembly in the usual way. No troubles are encountered with adhesion, and it is interesting to note that, within limits, the product in strip form can be rolled to size. Thus, if the phenolic paper strip is rather too variable in the strip, not being consistently obtainable to such close limits of thickness as aluminium, the zinc-coated material, if not excessively oversize, can be pulled through steel rollers set to the maximum dimensions. This " flows " the zinc, still producing a satisfactory product.

When essential for absolute cleanliness, metal-sprayed strip material can be interleaved between tissue paper for blanking and piercing to obviate contamination, and operators can wear cotton gloves. This extreme, however, is usually unnecessary if the tool is operated clean and " dry."

Fig. 10 shows some of these zinc-sprayed insulators taken from a bank assembly. Fig. 11 shows some of them which have been broken to show the absence of any tendency of the coating to flake away. Fig. 12 shows scratch test results on some of them.

While it is generally true to assert that metal spray coatings will only adhere to surfaces well cut, although finely so, by abrasive blasting, this is not always the practice. In some cases, satisfactory results are achieved without any prior preparation to augment adherence, while in others a lacquer or a varnish coating is employed. Such procedures are, however, strictly limited, and this fact cannot be too strongly stressed.

With glass radio valves, success has been achieved commercially by applying low-melting-point alloys, such as Wood's metal (melting point about 60 degrees C.), from an electrically heated spray gun, with no preparation of the glass. Adhesion is apparently good, although spells of trouble are encountered from time to time. The explanation is that the heating effect with such a low temperature spray is small, the metal forms a complete cylindrical envelope, it contracts on cooling a little more than the glass, and upon cooling forms a shrink fit. The troubles periodically encountered are due to conditions of temperature, thickness of coating and degree of contraction not being just ideal. On the whole, the procedure is a little chancy. At the same time, there is no reason why, in parallel

Table 21.—Laboratory Characteristics of Air Drying Clear Colourless Lacquers of the Cellulose/Glyptal Resin Combination Type.

	No. 1	No. 2
Compositional :		
Volatile spirit (loss in wt. 3 hrs. at 110°C.) %	91.3	78.5
Total solids %	8.7	21.5
	100.0	100.0
Ash on incineration %	Traces	Traces
Physical :		
Specific gravity at 25°C. ..	0.879	0.940
Viscosity at 25°C. in centipoises	12	225

For material No. 2, dilute 50/50 by volume with thinners for spraying.

Table 22.—Laboratory Characteristics of Thinners for Clear Colourless Lacquers.

	No. 1	No. 2
Specific gravity at 25°C.	0.825	0.875
Acid value	Nil	Nil
Composition. Per cent. by weight:		
Nitrocellulose solvent (butyl acetate)	45	21
Hydro-carbon diluent:		
Petroleum benzine	55	—
Coal-tar naphtha	—	61
Butyl alcohol	—	18
	100	100

cases, success of similar order with plastics should not be achieved.

Again, with radio valves, it is believed that the present-day practice is to use zinc applied by the wire or powder methods, with no abrasive blasting, but using a preliminary lacquering operation. The procedure is successful. The glass is first sprayed with a thin coat of cellulose lacquer, allowed the normal drying period, and then metal sprayed. Adhesion is excellent. The lacquers already quoted in Table 16, suitably thinned, are useful, although the thin combination cellulose-glyptal resin lacquers quoted in Table 21 are to be preferred. Thinners for the two types are illustrated in Table 22. Thin shellac or varnish coatings have also been used.

The organic coatings as a base for metal spray have been tried on metal work in general, for different metals and alloys, in different thicknesses, but, within the writer's experience, with no real success. They have been tried on the phenolic plastics, likewise without any success. Thus the strip material already referred to cannot be prepared in this manner; the zinc coating adheres to the lacquered surface reasonably well, but fails in the blanking and piercing operation, tending to flake away too easily.

Success of the lacquering on valves is probably again accounted for by the fact of a complete envelope of metal shrinking to hold itself in place, with the lacquer coating providing an elastic and compressible cushion. Therefore, it may be suitable on plastics of the same symmetrical shape as radio valves, but no commercial exploitation can be cited.

Of all the methods of metallizing plastics, these processes of direct application are, perhaps, the most important and have the largest future. The operations involved are "dry and clean," no aqueous solutions of chemicals, as in electroplating, are entailed. There are no chemicals to be retained by the material to spot out later. Pretreatments are not damaging, simple degreasing in solvent when oil and swarf have to be removed, and abrasive blasting. The metal spray is applied directly to the plastic, initial adhesion is maintained, and serviceability of the coating is governed by the properties of the metal itself.

When desired, the metal-sprayed coatings can be burnished or polished for appearance, and they can, in fact, be chemically coloured for decorative purposes. Thus, finishes such as oxidized copper, china bronze, florentine brown and so forth are practicable. Coatings have been electroplated by ordinary processes, but the need for such treatments is unusual and very specific in application.

The applications of metal-sprayed plastics are chiefly electrical or decorative. Other applications must not be overlooked however. There are many instances where metals are required, and in which weight can be conserved, yet still providing adequate mechanical strength, by using plastics having a metal coating from

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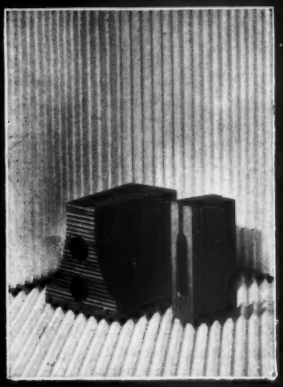

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0.001 in. to 0.005 in. thick. Much metal may thus be saved—an important feature to-day. The phenolic laminated sheets (paper, fabric or wood) and rods, rolled or moulded, as well as tubes and section, particularly figure in this field.

The requirements of those potential users who have not their own metal-spraying equipments can be catered for by industry. In this connection, it is pointed out that Messrs. Runcolite, Ltd., market a range of standard lines under the designation of "Metrelite" metal-coated synthetic resin bonded sheets. Grade P is paper laminated and F fabric laminated. Standard sheet sizes are 20 ins. by 40 ins., and thicknesses 1/64 in., 1/32 in., $\frac{1}{16}$ in. and $\frac{1}{8}$ in. Special sizes and thicknesses can be offered. Standard metal coatings are zinc both sides, aluminium both sides, and zinc one side with aluminium the other. Again, other metals, or combinations of them, can be supplied, including brass, copper, tin, cadmium, etc., while special thicknesses of metal coating can be provided. The base material, phenolic laminated, is in the usual high electrical grade. The coatings withstand cutting, drilling, punching and all forms of machining. Vibration tests have proved the coatings immune from deterioration, and electrical tests are claimed to establish the electromagnetic properties of the standard zinc-coated sheets to be equal to that of 0.02 mm. tin foil. Therefore, here is commercially available the finished product as a "raw material." Again, industrial metal spraying concerns are established that can execute work on stock or components to customers' requirements, and can include coating with weather-resisting synthetic resin solution.

(To be continued)

INQUIRIES AND ANSWERS

(Continued from page 384)

cleaner (metal or plastics); slicing machine operator; seasoning stover; scrap soaker.

10 Extra Coupons:

Maintenance electrician; tool fitter wholly employed in plastic production shop.

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Laminated Sheet

On p. 298 of the July issue of "Plastics" you mention that laminated tube and sheet materials made by impregnating sheets of paper are available.

I am anxious to get into touch with a firm which could impregnate paper for us in connection with plate making. Could you give me the names of one or two firms who do this? S. ENGRAVING CO.

[EDITOR'S NOTE: Flat sheets made by this process have long been available from concerns such as Bakelite Ltd., Berkley's Ltd., Bushing Co., Ellison Insulators Ltd., Micanite and Insulators Ltd., etc., Since the problem is apparently one of reproduction, that is block-making, or photographic (?), special raw materials may be necessary for "compatibility."]

Honeycombs

Would it be possible to produce honeycombs made of plastic materials? If a suitable moulding compound were found it would increase honey production greatly. G.M.G.

Norwich.

[EDITOR'S NOTE: At first sight this may appear merely an amusing inquiry; we are most interested and we have had several of the same nature. The main factor from the bee-keeper's point of view is that the bee wastes a large number of bee-hours in making the comb from wax and will make honey instead of wax if the comb is provided. It is interesting to note that reports state that bees will not lay honey at all in metal ones and will chew combs, fabricated from paraffin wax, to pieces with rage at the deception. The main job is to choose a suitable plastic (the problem may have something to do with odour). The moulding of a comb is not insuperable, for Ebonestos, Ltd., once produced a reflector that resembled one.]

Urea and Alkyd Resins in Water-Repellent Coatings

A WATER-REPELLENT coating having a synthetic resin base and designed for a specific application on metal-work is of interest not only with respect to its composition but also with regard to the possibilities of formulations of the same nature in other fields, and for non-metallic surfaces as well as for the metals. The particular mixture in question is designed for use on aluminium ice trays and grids for preventing the sticking of the ice. It is due to the General Motors Corporation and is covered by U.K. Patent No. 548,106 dated September 25, 1942.

The objects of the patented composition are to provide a coating mixture that adheres tenaciously to metal, that is sufficiently hard to be tough without being brittle, and that is water repellent to a degree to prevent ice from sticking to metal. Also, the provision of a coating that will not wear away appreciably during repetition usage is claimed.

The patent refers to the use of ice trays without the application of a superficial coating of water-repellent material, in which case it is necessary to melt the ice somewhat in order to eject it. It also refers to water-repellent coatings of waxes of the paraffin type that have been used to prevent the sticking of ice and for the avoidance of the ice-melting operation. Further, it indicates that these wax coatings, in order to improve the efficiency, and in particular to enhance their adhesion, have been applied to anodized aluminium surfaces. The pores of the oxidized film absorb the wax and hold the coating more firmly in position. Such coatings still exhibit excessive wear, and when the coating is partially worn off, it is little or no better than no coating at all because the ice still sticks at the bared area. The patent suggests 50 to 75 ejections as the maximum likely to be achieved with such coatings, after which recoating or warming has to be resorted to. The patented composition avoids the necessity for the anodic process and is claimed to give a life of three to four times that of the best of the wax compositions.

The composition comprises a high melting point wax (that is, one of melting point above about 140 degrees F.), a urea-formaldehyde resin, an alkyd resin and a solvent, with the total resin content between 50 and 90 per cent. of the total solid content by weight.

A preferred composition mentioned in the specification comprises from 2 to 30 per cent. of urea-formaldehyde resin and from 98 to 70 per cent. of alkyd resin, thermosetting type and solid at ordinary temperatures although thermoplastic alkyd resins may be employed. The patent explains that alkyd resins are the products from polybasic acids and polyhydric alcohols, the nature of the alcohol

Table 1.—Comparison of Stanolind and Paraffin Waxes.

	Stanolind	Paraffin
Specific gravity	0.920	0.902
Tack (room temperature)	Very slight	Little
Structure	Semi-crystalline	Crystalline
Solubility in organic solvents at room temperature	Very slight	Quite soluble
Penetration 100 grams at 75°F.	10.5	24.8
Empirical formula	$C_{36}H_{72}$ (approx.)	$C_{24}H_{50}$
Melting point (F.)	178°-181°	128°
Molecular weight	Greater than 500	346

Table 2.—Characteristics of High Melting Point Mineral Waxes.

Sample No.	Melting point degs. F.	Saponification value, mgms. KOH/gm.	Acid value, mgms. KOH/gm.	Ash %
(1) Superla	165	—	—	—
(2) R.O.W.2.. ..	162	—	—	—
(3)	169	—	—	—
(4)	178	—	—	—
(5)	176	1.2	0.5	0.04

determining for the present purpose the distinction between thermosetting and thermoplastic. If the alcohol contains only two hydroxyl groups, it yields a thermoplastic resin, whereas with more such groupings, a thermosetting product is obtained.

The resin mixture is mixed with the waxes, a mixture of carnauba and Stanolind being mentioned, using a solvent, and the mixture is applied to the ice tray and grid by a dipping and draining process. A suitable solvent mentioned is coal tar hydrocarbon such as benzene or toluene. The coated articles are oven heated to dry off the solvent and to polymerize the resinous product. This polymerization hardens the resin and contributes to the setting of the film, reinforcing the wax and increasing the life of the coating.

The Stanolind wax is a proprietary article, the name being a registered trade mark. It is a hydrocarbon wax obtained from crude petroleum, being denser, less crystalline, more tacky and higher melting than paraffin wax. The patent gives comparative characteristics of the two waxes, and these are reproduced in Table No. 1. Stanolind wax appears to be of closely similar nature to the high melting point mineral waxes used in the electrical industries for coil impregnation and for the manufacture of fixed paper condensers, e.g., Superla wax and R.O.W. 2 wax (Messrs. Claude Campbell and Co.). Some characteristics of these are given in Table No. 2.

The alkyd resins may be of the modified type in which drying oils, semi-drying oils or non-drying oils are employed as the modifying agents. Partial oxidation then occurs during the oven-drying stage. As a specific example the following is cited:—Solution A. 90 gms. of mixed resin (urea-formaldehyde resin plus alkyd resin or oil-modified alkyd resin) are added to 410 gms. of a suitable solvent, e.g., a coal tar hydrocarbon, and stirred to dissolve. Solution B. 15 gms. of Stanolind wax and 5 gm. of carnauba wax are mixed with 300 gm. of the coal tar derivative solvent at a temperature of about 300 degrees F.

Solution B is cooled to about 150 degrees F. and solution A added slowly with stirring. The ratio of resins to waxes is thus 4.5 to 1 in the final product.

In use, the process is to dip the articles, drain, and oven dry for 30 minutes at 300 degrees F.

Urea resin alone gives a hard coating that tends to be brittle. Alkyd resin alone is tough but tends to be soft. By discreetly blending the two, a predetermined degree of hardness may be obtained to suit any conditions desired.

The Stanolind and carnauba waxes are preferred as the wax ingredients, although high melting point paraffins (about 140 degrees F.), high melting cerese wax, or any of the high melting point synthetic waxes, may be substituted for the carnauba. The success of the coating, however, is largely determined by the polymerization of the synthetic resins in the mixture, hardening and reinforcing the wax to resist wear.

The claims of the patent are:—

(1) A water-repellent coating composition comprising a mixture of high melting point wax, a urea-

formaldehyde resin, an alkyd resin, and a solvent, the resin content being between 50 and 90 per cent. by weight of the solid content.

(2) A water-repellent coating as in (1). The wax ingredient being carnauba wax, Stanolind wax, or a mixture of the two.

(3) A water-repellent coating mixture comprising a solution of 2 to 30 per cent. urea-formaldehyde resin, 98 to 70 per cent. alkyd resin, and Stanolind and carnouba waxes in the ratio of approximately 4.5 to 1 of resins to waxes.

(4) A method of coating an aluminium ice tray by making a solution of urea-formaldehyde and alkyd resins, Stanolind and carnauba waxes, in coal tar derivative solvent, coating by immersion, draining and drying at about 300 degrees F. to dry-off solvents and to heat-harden the resins.

(5) Aluminium ice trays coated with heat-hardened compositions claimed in 1 to 3.

The urea resins and the various forms of alkyd resin of the glyptal group are already used extensively, alone or in combination, for metal-finishing purposes, both for decorative and protective purposes. The ureas form the basis of many glues and adhesives especially for wood. Various synthetics are used in textile finishing, for numerous purposes including water repellency. The balanced mixture of resins, virtually plasticized with wax, covered by the patent referred to above, illustrates another problem catered for by the synthetic resins.

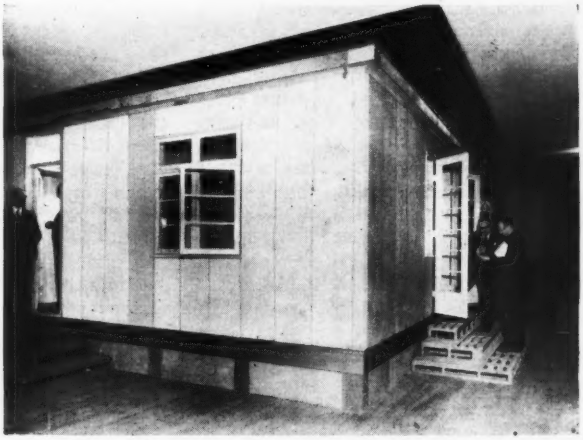
PREFABRICATED HOUSE EXHIBIT

On the 28th August an interesting exhibition incorporating a factory-produced bungalow was shown at Conway House, Bloomsbury, by Tarran Industries, Ltd.

Erroneously called the "All-Plastic House" by our daily papers (in fact there were no moulded plastic structures at all), it was nevertheless an extremely interesting and valuable lesson in modern time- and labour-saving construction of building.

From the plastics point of view the main interest lay in standard floor or roof panels, 12 ft. by 4 ft., made of resin-bonded plywood sheets, 12 mm. thick, supported by joists of the same material. Walls are of Lignocrete (sawdust-cement type) fitted in ribs of resin-bonded plywood ½ in. by 3 ins. A complete floor using the above units was laid by 8 men in 7 mins.

All panels are bolted together in the construction of the walls, floors or roof and bonded with a bituminous jointing.



Prefabricated bungalow. Resin-bonded plywood is widely used in the construction.

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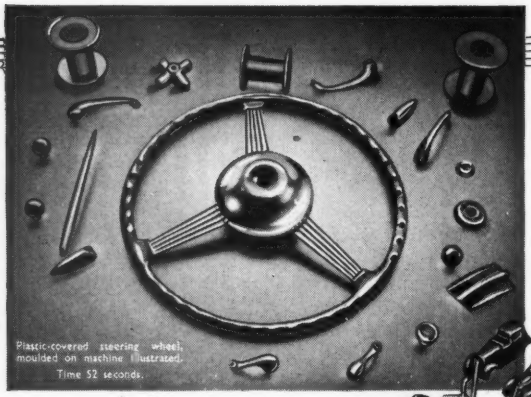

Plastic-covered steering wheel, moulded on machine illustrated. Time 52 seconds.

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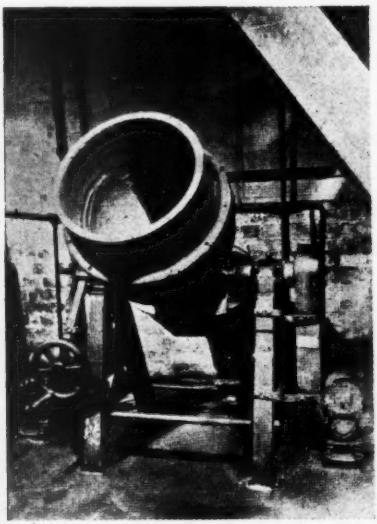
PRODUCTION NEWS

Raw Materials, New Plant, Works Organization, Control Apparatus, Research, Personal and Trade Notes

TUMBLING BARRELS.—One of the most widely used items of production equipment is the tumbling or shaking barrel. It is used for polishing and burnishing, removal of scale, eradication of sharp edges from components and parts and other cleaning-up processes.

It is used in the metal-working trades generally, ferrous and non-ferrous, and particularly the cycle, car and aircraft factories and in works which manufacture components from wire and rod. It is also useful for many plastics and ebonite.



In the design of such barrels, great care has to be given to the loads created by the work and its varying positions, particularly in tilting. An improved type of barrel has recently been developed by W. Canning and Co., Ltd., Birmingham. The main portion comprises a heavy cast-steel open-mouthed barrel fixed to the top of a substantial steel shaft, supported on trunnions which are co-axial with the horizontal bevel pinion shaft.

The barrel is spigotted to the upper face of a bevel gear to which it is firmly attached by heavy set bolts. The bevel gear is keyed to the upper end of the shaft and additionally secured by a flush-fitting lock nut. The heavy bevel gear, which is protected by an efficient steel guard, engages with a bevel pinion mounted horizontally on Fischer bearings. The vertical shaft revolves in two robust Timken tapered roller bearings, the lower and larger one of which carries the whole of the thrust due to the weight of the work, barrel, spindle, etc.—often a very substantial thrust indeed.

The weight of the barrel and its contents is balanced by a weight, the position of which can be varied to suit the weight of the work actually being treated.

The vertical shaft bearings are carried in a heavy cast-iron housing provided with a trunnion mounting which is central with the horizontal bevel pinion shaft. The barrel can thus be revolved about the horizontal axis and normally runs at an angle of 30 degrees from the vertical.

Barrel tilting is effected by hand-wheel control operating through a worm gear which rigidly holds the barrel in correct working position without other lock. Allowing for swing of the barrel to its lowest position, the overall depth is about 58 ins., the width across the front at ground level being about 60 ins.

The machine is chain driven by a 2 h.p. electric motor for 440 volts 50 cycles three-phase operating via a rib-cooled worm reduction gear unit of 1,420/100 r.p.m. The barrel speed is 50 r.p.m.

PUMPING VERY HOT LIQUIDS.—One of the most difficult general applications of the centrifugal pump is the handling of very hot liquids, of which an example is the pumping of high temperature water in connection with process work, pressure heating circuits, and thermal storage tanks, whilst there are many others in the chemical and carbonization industries.

Pumps for such services have to be capable of withstanding not only the high temperature but also the pressures involved, so that water-cooling, if necessary, as well as careful design to prevent leakage from the gland, especially as in the case of hot water flashing to steam takes place.

In this connection the Pulsometer Engineering Co., Ltd., Reading (Berks), has available two special "JA" and "JB"-type pumps in which gland trouble is reduced to a minimum by mounting the hydraulically balanced impeller overhung on a wide diameter shaft, so that only one gland is necessary. Water-cooled bearings and stuffing boxes are also provided, and to preserve alignment at varying temperatures centre-line suspension is adopted. With a hood of ordinary design the rise in temperature would be sufficient to affect the alignment, but in the case of centre suspension having the supporting lugs close to the water jacket little heat is transmitted to the bearers on the baseplate.

The range of these pumps covers duties up to 3,000 galls. per minute and working heads up to 180 ft., with working pressures up to 300 lb. per sq. in. and corresponding hydraulic test pressure of 450 lb. per sq. in. and water temperatures up to 400 degrees F. With modifications to the standard design, it may be stated that oils and tar fractions having a high vapour pressure are also being successfully handled at temperatures even as high as 650 degrees F.

In the case of high temperature water, since any fracture would result, as already stated, in flashing into steam, the casing and back cover of the pump are made in cast steel, the ductility of which makes it a far more suitable material than cast iron, although for some conditions other metals, such as bronze or high-tensile iron, may be used. Hot liquids up to 212 degrees F. (100 degrees C.) containing acids can also be dealt with by the "Pulsometer-Doulton" stoneware centrifugal pump, a joint production with Messrs. Doultons Ltd., suitable for all acids except hydrofluoric as well as other liquids having a corrosive effect on metals. These include sulphuric, nitric, hydrochloric and sulphonic acids.

PRODUCTION BULLETIN.—The August issue of "Production and Engineering Bulletin," published by the Ministry of Labour and National Service and the Ministry of Production, contains many items of exceptional interest to all works managers. Among these are: Quality Control Charts, Machine Tool Control, Scrap Campaign, Practical Methods of Segregating Steel Swarf, Alternative Method of Machining a Curved Surface, Storing of Grinding Wheels, Women in Tank Construction, Personnel Management, etc. Each article is profusely illustrated with photographs and excellent charts.

"MITIA" COLOUR CHART.—We have received from Thos. Firth and John Brown, Ltd., a copy of their new "Mitia" Carbide Grade Colour Chart. Giving, as it does, a list of recommended applications, and also instructions on the care and maintenance of "Mitia" Carbide Tools, this should prove a valuable guide to the many operatives who now make use of these hard cutting alloys, and is, of course, designed especially for workshop use.

THE MINISTER OF SUPPLY, Sir Andrew Duncan, stated recently in Parliament that it would not be in the public interest to disclose the name of the product to be manufactured by the new subsidiary company of British Celanese known as Celanese Plastics Development, but he gave the assurance that its use would be controlled by the Government for approved purposes.

BRITISH INDUSTRIAL PLASTICS, LTD., has entered into an agreement with Elliotts and Australian Drug Proprietary, Ltd., for the formation of a company to be called Beetle Elliott Proprietary, Ltd., for the manufacture and sale in Australasia of beetle resins and moulding powders. Licences have been granted to Imperial Chemical Industries, Ltd., for the manufacture of aminoplastic materials under patents controlled by British Industrial Plastics in Great Britain and Europe.

PERSONAL

Mr. A. Scotting, late of Kork-N-Seal, Ltd., has been appointed manager of the Moulding Division of the United Development Assoc. (Plastics), Ltd., at its No. 3 Factory, High Wycombe.

Mr. A. J. Gibson, Special Officer Lac Inquiry, at India House, relinquishes his duties under the Indian Lac Cess Committee on September 15, 1943, and from that date becomes Technical Adviser on Shellac to the Ministry of Supply.

The Indian Lac Cess Committee has reorganized the London Shellac Research Bureau. The post of Special Officer Lac Inquiry will be abolished. The main staff will then consist of a Director (Dr. B. S. Gidvani to act pending further instructions), with a Lac Information Officer under him (Dr. B. S. Gidvani to act in this post also, pending arrival of a permanent incumbent from India).

The Lac Research Laboratory will remain in Edinburgh for the time being.

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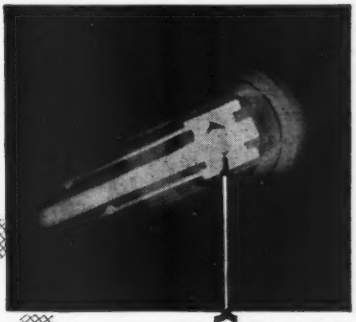

Radiograph of moulded assembly showing incorrect location of metal insert.

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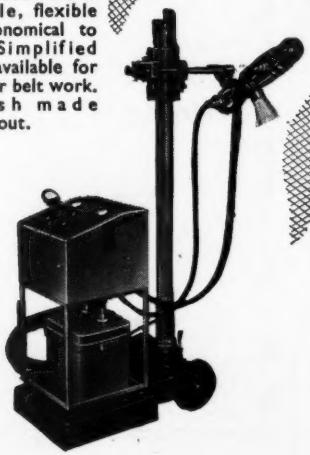

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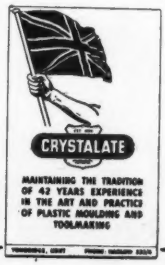
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BRITISH PATENT ABSTRACTS

554,737.
Application: 19.2.42.
Granted: 16.7.43.

Improvements in and relating to manufacture of Reinforced Plastic moulded bodies. English Textilose Mfg. Co., Ltd., and F. Moss.

In the manufacture of cloth impregnated laminated plastics there is a danger of having air trapped between the layers of cloth. To overcome this woven paper fabric is impregnated with a phenol-formaldehyde plastic, the openings in the weave being sufficiently large to allow the air to be expelled when the laminate is pressed.

554,529.
Application: 2.12.41.
Granted: 7.7.43.

Improvements in Decorative Panels. R. R. Hoare.

Where it is desired to make a number of decorative or advertising panels of the same design, the latter is transferred in relief under heat and pressure to a thermoplastic sheet so that the design appears in reverse. This sheet forms a mould which may subsequently be used for casting plaster, clay or other plastic materials.

554,540.
Application: 29.1.41.
Granted: 8.7.43.

Improvements in and relating to composite Friction Articles. General Motors Corporation.

The method of making a friction article consists in sintering a non-compacted metal powder to a metal backing sheet impregnating the porous matrix so formed with a thermosetting resin and heating with pressure to bind the whole together to form a rigid layer of friction material.

554,602.
Application: 7.11.41.
Granted: 12.7.43.

Improvements in and relating to Electric Insulation. Standard Telephones and Cables, Ltd.

In order to overcome the disadvantages of polystyrene when used as an insulating cable covering at low or high temperatures a polyhalogenated derivative of hydrocarbon which is symmetrical about its centre of gravity and is either (a) a single ring aromatic hydrocarbon, (b) an aliphatic hydrocarbon, or (c) an araliphatic hydrocarbon in which the halogen atoms are disposed symmetrically. The compound so produced will have a molecular weight of between 160 and 600 and is used in proportions varying from 1 to 15 per cent. by volume (when the substance is liquid at 15 degrees C.) or 1 to 20 per cent. by weight when it is solid at this temperature. Examples of the halogenated compounds used are 1.1.2.2. tetrabromoethene, 1.3 di-iodopropane.

554,703.
Application: 17.1.41.
Granted: 15.7.43.

Phenolic Resin Compositions and method of making same. Haveg Corporation.

The addition of dyes for the determination of the end point of a heat hardening resin reaction is already known, but this patent claims the addition of a dye in conjunction with a filler such as finely divided quartz to indicate the distribution of the hardening agent in an acid catalysed resin. One example given is the use of Metanil yellow and quartz. On adding sulphuric acid a deep purple colour is obtained.

554,718.
Application: 10.9.40.
Granted: 16.7.43.

Manufacture of delustred or Pigmented Synthetic linear polyamides. Du Pont de Nemours.

Difficulties have been experienced in the past in delustring or dyeing synthetic linear polyamides, e.g., Nylon, by the addition of finely divided pigments to the melted mass of material. In this patent the pigment is added to the reaction mass before any marked increase in viscosity has taken place, agitation being secured by the ebullition of the mass.

Resinoids and Other Plastics as Film Formers

By B. J. BRAJNIKOFF,
Consulting Electrical Engineer

XX.—Problems of Polymerization

THE problems with which the plastics technologist is faced to-day are essentially the fundamental problems that confront the physical chemist, viz., those associated with the new paths of the modern physics in the realm of the atoms and molecules and the examination of the dynamics of chemical reactions. The task of the physical chemist is to provide a consistent theory of the chemical process, a theory which, in the hands of the chemical engineer, would enable him not only to bring the production process to light, but would also reveal its new possibilities.

The notable advances made recently in the studies of the surface phenomena, flotation, electro-capillarity, the nature of the electrical double layer, adsorption, activated adsorption, surface tension, the origin of sorption forces, all enable the technologist to tackle such important practical problems as the preparation of superior coating media, film-forming and impregnating agents, and a great diversity of other compositions.

Closely connected with the electro-capillary phenomena are the problems of electro-chemistry, the electrode processes, over-voltage, passivation, etc., which are of great interest to the plastics technician in the field of electro-deposition of resins, surface treatment, electro-impregnation, and numerous other galvanoplastic processes already dealt with.

Of equal importance to the plastics worker are the problems of quantum chemistry, the questions of the homo- and heteropolar chemical bonds, the structural-valency problems, the dielectric properties of molecules, spectroscopy, which is meeting chemistry through the Raman effect; photo-chemistry and the application of high- and ultra-high-frequency electric currents, as has already been emphasized on several occasions in previous sections, are of special value in plastics technology, since they permit realization of a great number of processes, as, for instance, those based on polymerization, with efficiency and qualitative results superior to many other techniques.

The Development of the Polymerization Reaction

It is comparatively not very long ago that high polymeric compounds were regarded as inaccessible to investigation; the very process of the polymerization itself appeared to be extremely obscure. The organic chemist had invariably referred to the proverbial " resinification " of the reaction products as a stage where further study becomes already impossible; the polymerization process was originally considered as a nuisance and an obstruction to research. Even those investigators whose primary concern was the study of polymerization were content with such results as the qualitative registration of the fact of the occurrence of the process under the influence of one or another physical agent (light, radio-active emanations) upon the substances already known for their ability to polymerize, or sought in a crude empirical manner for suitable components, whose interaction would yield a polymeric product.

One approach to the problem has been displayed by those who have examined, mainly, not the polymerization as such, but the final polymer. They have accumulated a voluminous fund of factual data, but, naturally enough, in the absence of knowledge concerning the factors promoting the polymerization, they were unable to furnish any other informa-

tion save a few empirical rules of a qualitative character. For example, they have stipulated that substances which contain the carbonyl group, or the molecules possessing the conjugated double bonds, are easily polymerizable. But, since there are readily polymerizable bodies having neither carbonyl group (e.g., diolefines) nor conjugated double bonds (viz., cyanogen), it is evident that the scientific value of such rules was very limited.

Furthermore, organic chemists have always treated the polymerization as an ordinary chemical reaction. The peculiarities of the process received no due consideration, and the attention of the investigator was not focused on the interpretation of its specific features.

The period that followed the war of 1914-1918 was marked by a drastic change in the attitude to the high polymeric studies: from an obscure, hardly known corner of science, they have been transformed into a realm of the utmost importance, attracting the closest attention of chemists and physicists. The extensive application of X-rays and other physical methods imparted to researches on polymerization an entirely new tempo.

This drastic change is a typical instance of the inalienable unity between science and technology. When the scientific aspects of the polymeric products were little known, the latter had no chance of being used in the industry, and hence the stimulus for their study was almost absent. But the tremendous importance attached during the past two decades to such materials as various plastics, synthetic coating and film-forming agents, impregnants, cements, and endless other products, have given rise to the need for a theoretical grounding of these vigorously growing branches of industry. A specially beneficent factor in accelerating the studies of high polymers was the importance attached to researches on the new substitutes for the vehicles of the different varnish systems (viz., boiled oil and the like) and the formulation of the theory of film formation; the information gained therefrom concerning the utility of various synthetic polymers, such as elastomers, resins derived from petroleum and coal, etc., greatly helped in enlarging the assortment and the quality of diverse polymers, some of which proved to be even better suited for the manufacture of the film-forming and kindred media, than the natural products themselves; this may be illustrated by the concrete example of the application of latex-like impregnants now being used on an industrial scale.

Synthetic Latex Impregnants

The importance of the latex-like systems may well be instanced by their application to impregnating processes as developed lately in the manufacture of moulded brake lining materials for the automotive industry.

There are two main kinds of brake lining used in motor cars: (1) the woven fabric of asbestos and brass wire yarn and (2) the compressed asbestos board. The brake lining of the second type is produced from a special grade of asbestos sheet, usually impregnated with a solution of linseed oil in white spirit. However, the existing mode of manufacture of the pressure-moulded brake board has many substantial drawbacks, viz., a very long multi-stage process with about 18 operations; the application of linseed oil as the binding medium requires expensive white spirit as solvent; the fire-hazards of the impregnation procedure; finally the quality of the linseed-impregnated asbestos products does not fully meet the exacting demands of the industry.

The latest researches in Russia have proved that by using an artificial latex (preferably based on divinyl) as an impregnant in place of linseed oil, it is possible to effect an appreciable production economy, due to shortening of the number and the length of operations, and turning out much better quality brake lining material. The principal merit of the synthetic latex as impregnant is its ability to be well distributed over the surface of the asbestos fibres and bonding

them into a strong homogeneous mass throughout the thickness of the body, thereby assuring the stability of the physical characteristics of the brake lining material in general and the friction coefficient in particular. Another favourable factor in applying latex-like compositions to the making of the brake lining is the property of the asbestos to adsorb inorganic substances, if they consist of highly dispersed particles and have not too high a specific gravity.

The latex-like impregnants for the manufacture of brake lining, as developed above, were preferably based upon divinyl rubber, which amounted to 15 to 20 per cent. (by weight) of the system; instead of divinyl derivatives, co-polymers of the butadiene plus styrol, or any other suitable combination may be used with good results.

The Technological Procedure

The mass is treated on the roller mill, which performs the preliminary splitting off of the asbestos into elementary fibres; after introducing a filler (e.g., zinc oxide, barytes, kaolin, etc.) and a vulcanizer (if required), a latex emulsion is then poured into the roller mill. By spreading uniformly over asbestos filaments, synthetic latex is coagulated there by virtue of the contact with the oppositely charged asbestos.

The mass thus prepared is passed into a mixer, where it is diluted to a desired concentration and is transferred to the cardboard-making machine, which turns out sheeting material of different thickness depending on the overall size of the final product to be obtained.

The cardboard, thus produced and liberated subsequently under the pressure from the excess of water, is then ready for punching of the brake lining segments of suitable design. These punched details of the brake linings are then dried in an oven of the chamber type (which with greater advantage may be replaced by the high-frequency electric heating) at definite temperature, and are subjected to pressure on a hydraulic press. Recent investigations have shown that the percentage of the permanent set of the impregnated material obtained under the pressure has a great influence upon the physical and mechanical properties of the brake lining stock.

After the pressure treatment the material is cured in an oven of the tunnel type, carried through on the conveyor (in this case, again, the curing may be effected by the inductive heat derived from a single-phase inductor), and after polishing is ready for testing.

The technological procedure for the making of brake lining material based upon synthetic media is appreciably simpler than the production scheme with linseed oil as impregnant; thus, for instance, instead of 18 to 20 operations requiring 12 days with the oil base, it takes only three to four days to complete the process with divinyl latex medium, using relatively simple plant.

The Test Results

The quality of the brake lining materials based upon synthetic latices may be judged from the extensive tests carried out by the experimental department of the largest automobile works in Russia, at Gorky, on the Volga River (designed after the Ford's plant at Detroit, U.S.A.). The principal types of the examined products included: (i) the standard moulded brake lining using oil as base; (ii) woven asbestos-wire model; (iii) moulded synthetic latex impregnated brake linings (four variants). After exhaustive tests the following conclusions were reached:—(a) The standard moulded brake linings with an oil base display markedly low capacity for resistance to abrasion, leading rapidly to appreciable wear and tear of the brake drum. Particularly drastic is the action of water upon the friction surfaces. The brake performance parameters are not high; there is a loss of smoothness of the brake operation after a relatively small number of brake applications (of the order of 100), i.e., the onset of rigidity on braking due to the loss of the elas-

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ticity of the friction lining, the brake operation, starting from the speed of 30 kiloms. per hour, is aggravated by vibrations; the penetration of water, oil, grease and temperature changes cause slipping and instability of the brake. Moreover, the brake lining segments based on linseed oil exhibit poor strength properties, as has been demonstrated by numerous breakages sustained during the testing.

The foregoing tests revealed that the overall characteristics of the brake lining materials based upon synthetic latices are superior to any other make, particularly in comparison with the standard specimens of the brake linings with an oil base. The moulded latex-impregnated brake lining is highly resistant to heat and moisture, and its outstanding advantage is that the friction is very uniform, giving smooth, quiet working, and is, therefore, better fitted for heavy duty. A further advantage of the brake lining made with synthetic latices is that it can be worked to closer limits than other stock, easily and accurately fixed, adjusted or replaced and kept in the best possible conditions, thus ensuring a longer serviceability and the safety of the car.

The Basic Concepts of the Polymerization Process

From what has been stated earlier it, naturally, follows that among the most urgent tasks of the polymerization process is, first, aiding the plastics chemist by transferring a part of his research burden on to the shoulders of the physicist; secondly, supplanting the blind empiricism by an entirely methodical approach to the whole problem; and thirdly, a complete reconstruction of the fundamental notions on the polymerization reaction.

The object of the traditional organic chemistry is to obtain an individual substance in the state of absolute chemical purity, whereas a polymer is not, generally, in its essential aspects an individual body. We always have in it a mixture of molecules of various degrees of the polymerization, containing a number of monomeric units which is capable of varying within a wide limit. There is no means of isolating the individual components of such a mixture not only technically but even in principle, since to every sum total of the physical conditions corresponds not a single of the components, but one or another dynamic equilibrium in the molecular structure (of course, in the "true" chemical combinations we are also dealing with equilibria, but their nature is very different). For this reason the efforts of organic chemists to derive a polymeric substance in an individual state, as well as to determine its molecular weight and its chemical formula, are fruitless. The very notion of the "molecule" in this respect loses its meaning. For example, in polystyrols Staudinger[204] has established the existence of "molecules" comprising no less than 200 to 300 thousand of the units of the monomer, combined by the primary chemical valency bonds into a single chain.

In the case of the polystyrene, we obtain a mono-dimensional filamentary unit, having in the two directions the size of the molecule, and in the third direction—that of a microscopic body. However, in many other instances the combination of the molecules is effected not necessarily in the chain-like pattern, that is, in one dimension only. Kurt, Mayer and Mark[205] have demonstrated that, should the molecular constitution permit, it increases its length in all three dimensions. The remotely situated parts of the molecule form at the various points the new bonds, or between them there is built up a "bridge" by means of the oxygen or other "foreign" atom, united by their different valencies with the different parts of the molecule. By this process a "macromolecule" is formed, in which all atoms are combined through the chemical valence bonds, but not by van der Waal's forces, which have microscopic dimensions. In the limiting case, an entire giant polymer may represent one single molecule, what we have

almost certainly in many plastic masses, as typified, for instance, by the phenol-formaldehyde class of resins (Bakelite, etc.), which, in Staudinger's opinion, possess this structure.

For a long time there was a gap between the notions of the molecule and that of a microscopic body, which appeared to be without any transitional form of the matter between them. This gap has been filled in by Negheli, who proposed the concept of a micelle or crystallite. Notwithstanding its approximate, not well-defined character, this idea has been rooted up in the chemistry like dogma. For example, Ostwald asserts that the colloidal properties of substances are determined solely by the degree of the dispersion or, what is the same thing, by the degree of the molecular aggregation. Meantime, in the colloidal polymers we have no molecular aggregates at all as an inevitable intermediate form between the molecule and the microscopic body but a continuous process of manifest new quality—that of the microscopic body of a polymer—by the mere quantitative addition of the monomeric units.

For the reasons stated above, it must then be obvious that, as an example, the numerous works dealing with molecular weights of high polymeric compounds, determined by the cryoscopic and ebullioscopic methods, have been misoriented and were bound to lead to the discordant and divergent results. It is clear, therefore, that the organic analysis is as inapplicable in the studying of the constitution of high polymers, as all the other methods and concepts of the classical chemistry.

On precisely identical grounds these works must be regarded as erroneous, if they have been prompted by the idea to find at all costs in high polymers the micelles with the aim of explaining their colloidal properties, as, for instance, the earlier works of Mayer, and also those of Pummerrer,[306] who, with this object in view, have erected highly speculative structural schemes for the interpretation of their experiments.

Only on the basis of the complete abandonment of the antiquated notions, which fail to take into account the qualitative features, and replacing them by the new ideas of the macromolecule and the molecular mixture, is it possible to correctly conceive and carry out the experiment.

Chemical versus Physical Forces

The tradition of the 19th century was to oppose the chemical (inter-atomic) and the physical (inter-molecular) forces as belonging to the two absolutely different kinds. At the beginning of the 20th century it appeared, on the contrary, that every distinction between both kinds of forces had lost any meaning. At the present time we know that neither viewpoint proved to be correct. The chemical bond in homopolar molecules, according to London and Heitler, is an antisymmetric coupling of the electrons belonging to the two combining atoms and forming a special saturated envelope.

The intermolecular forces are of entirely different origin. As postulated by Debye, they are produced by the dipole moments of the molecules and are the sum of the two addenda: (i) a simple mutual attraction of the dipoles, and (ii) the mutual polarization of the molecules, if their charges are movable. With the aid of simple calculations, this theory affords the estimation of the value from the van der Waal's equation of state, with the concordant results in regard to order of the magnitude.

The inter-atomic forces of cohesion in the molecules represent the values, which are almost independent (for each pair of the atoms) of the general molecular structure. Analogously, the inter-molecular forces are the sum of the values of cohesion for the separate groups of the atoms in the molecule, effected in nearly additive manner. For the discrete molecules, the inter-molecular forces of cohesion vanish before the inter-atomic forces, and only the latter determine the chemical mechanism of the process, one or another course in the formation of the product, the configuration of the molecule, dynamic equilibrium, etc. While

the physical forces evoke condensation and, further, association, solvation, gelation and other related processes, which may be unified by a general term of aggregation, which includes also colloidal phenomena.

A totally different state of affairs is taking place in the polymers. The forces of cohesion, in so far as they are additive factors, may be considered as proportional to the length of the molecule. The experiments of Staudinger on the viscosity of polystyrenes, and many others, confirm this conception. Hence the molecular length in polymers may reach such a value that the physical forces, proportional to it, attain the magnitude of the chemical forces and exceed them. The direct manifestation of such a possibility is seen, for instance, when a part of the polymeric body, consisting of the thread-like molecules oriented in the parallel fashion, reveals a lower tensile strength along the threads themselves, i.e., against the inter-atomic forces, rather than in the direction at right-angles to the filamentary complexes, that is, against the inter-molecular forces.

The process of the polymerization is a resultant of a very complex interaction of both kinds of forces, where neither kinetics nor the ultimate formula of the product are conditioned by the valencies alone.

The Forces Involved in the Polymerization Process

The invalidity of the stoichiometric laws to polymerization and, following therefrom, the inconsistency of cryoscopic ebullioscopic and elementary analysis, and other chemical methods, necessitate the application of physical analysis—X-rays, electronography, mass-spectrography, etc.—as a better tool for the examination of the molecular structure. Nevertheless, even here it is essential to take into consideration all the specific features of the problem.

The X-ray analysis arose and developed through the investigation of relatively simple forms of matter: the heteropolar crystals. The simplicity of laws derived from such studies is explained, first, by the rigid bonding of the lattice elements, remaining at rest, and, further, by the exceptional geometric regularity of the crystal lattice itself.

In the " crystals " of polymers these simplifying conditions are lacking. The structural units greatly vary with regard to sizes, orientation, so that the lattice nuclei are directed only in a very rough fashion. Moreover, in consequence of the peculiar nature of bonds, the elements possess a far higher mobility, exhibiting in this sense the transition from the ionic lattices to liquids, thus confronting the investigator with one of the most puzzling aspects of high polymeric studies.

At the same time, in the amorphous masses of polymers, where we are dealing with a mixture of macromolecules combined by physical and chemical " bridges," the absence of strictly discrete molecules imposes upon the worker the necessity of exercising a particular care in the interpretation of results, clearly realizing that here, again, there is the need for the revision of the notions on the structure, orientation, lattice, nucleus, unit, etc.

The evolution of the molecular concept in chemistry originated and based itself on the following argument: if we go on dividing continually a given quantity of matter, one is bound to arrive ultimately at such a stage of operation, when the elementary amount of the substance does not permit of a further subdivision without changing its chemical properties. In crystallography, by means of a similar mental experiment—a successive division of the crystal into parts—there has been evolved an idea of the elementary body, the primary structural unit, still retaining all the properties of the macroscopic crystal, which formation was frequently termed the molecule of crystal. The elementary body was thus represented by a period of identicity, determined by that distance over which it was necessary to travel in the crystalline medium, in order to arrive at the point of its recurrent identical arrangement.

But, just as there are no molecules of polymers, so in precisely similar manner and for the same reason there do not exist the true elementary bodies within their masses. The elements of symmetry here constantly lose their regularity; perhaps the time is ripe already when it would be proper to put on the agenda the suggestion for the creation of a new crystallography of polymeric structures.

Chain Mechanism of Energy Transmission

The question, which is of the utmost importance to the studying of the polymerization kinetics, whether or not the polymerization process is of the chain-like nature, so far has not been adequately illuminated in the scientific Press. Here again, attention should be drawn to the confusion of ideas: the reference to polymeric chains, chain molecules, is frequent, but invariably this term is meant to convey the concept of the chain-like configuration of the molecule, its composition through the linking of the monomeric units, but nowhere is the question raised of the chain-character of energy transmission during the elementary act of the polymerization, i.e., in the sense of the chain theory of the kinetics, as recently developed by Professor Semenoff[307] in Russia, who definitely classes the polymerization as the chain process. It is universally known and recognized that the chain mechanism of energy transfer in nature is of a very wide occurrence. Such a mechanism, in fact, was proved for many photo-chemical and thermal processes for both the gaseous and liquid phases, when in the latter cases the number of links in the chain may reach and exceed the order of 10^8 units.[307]

The results of a series of experiments performed by Rubanovsky[308] on the polymerization reactions under the action of the electric discharge make it very probable that the polymerization is a process of the chain-like nature (that is, developing in the chain-like fashion). It will suffice here to mention one fact established by him, that during the polymerization of butadiene, evoked by the discharge, there takes place a "period of induction" of a few minutes, i.e., the time interval required, obviously, for the accumulation of an appreciable amount of the active centres of the polymerization. The existence of such an induction period is highly characteristic of the majority of chain reactions. The same inference can be deduced from a number of theoretical considerations, which will presently be analysed in more detail. In this connection it is necessary to recognize the inapplicability of the unqualified acceptance of the ideas of the chain theory to the processes of polymerization. Here, once more, the introduction of the rigid notions is just as inadmissable as the ignoring of the specific features of the process may from the start misguide the thought of the investigator.

In the case of an ordinary chemical reaction, the course of the development of the chain in a gas is perfectly analogous to the progress of the diffusion of the gaseous molecule, with the sole difference that either one or another active centre, in turn, functions as the diffusing particle.

Here, in estimating the length of a chain it is permissible to regard the molecule of the reaction mixture as static and the elementary portion of energy (the active centre) as moving. On the other hand, in the event, when there occurs, as an elementary act, the lengthening of the molecule, which even prior to this has already attained a giant size by the addition of the monomeric unit, the course of the reaction proceeds, to a certain degree, in the opposite way. The velocities of molecules are proportional to the square roots from their masses, and hence those of the polymeric molecules will be so small that, compared to the molecules of the monomer, the macromolecule may be considered as static. At one or both ends of the macromolecule there exists a portion of the energy of activation (in what form—this is a separate problem). The

molecule of the monomer, moving with high speed from the volume of the system, through the impact with the active end of the molecule, effects the elementary reaction, as a result of which the energy of activation migrates again at the end of the chain, being displaced over one of its link-segments.

This may be expressed by the following formula, illustrating the case of butadiene:

$$(C_4H_6)_X \cdot C_4H^* + C_4H_6 = (C_4H_6)_{X+1} \cdot C_4H^*,$$

where H^*— is the active end of the molecule of a polymer. In consequence of the above, the basic Semenoff's formula for the number of elementary reactions $\nu = \frac{6\pi^2}{4\lambda_0^2}$ (A) (B) is found inapplicable, as well as a series of the equations of more special character.

The problem of the fundamental significance as to the nature of the active centres of the polymerization, has also not been tackled hitherto.

In the capacity of the active end may function the molecular residue (the radical), further, the unsaturated valency of the disrupted double bond (as it probably occurs in the case of the butadiene molecule), finally, the molecule with the stored energy in the form of the transference of electron to the outer orbit, quantarotational energy, etc. All these possibilities can be realized in different chemical substituents and even in one and the same substance, depending upon the character of the exciting factor (e.g., impact of the electron, the ion). It may be noted that for the chain theory of the polymerization this plays the role of the utmost importance. The energy balance of the elementary reaction determines the probability of its realization. If the quantity of energy, concentrated at the active end of the molecule, appreciably exceeds the energy of activation, the probability of the reaction will be near to unity, if not, then it will serve as a determinant of the probability value. It is quite possible that the nature of the active end of the macromolecule may be considered as a rational basis for the classification of the types of the polymerization reactions.

The scanty information on the study of the potentials of the excitation and ionization for the organic molecules hinders this work, but does not render it infeasible.

Statistical Theory of Condensation (Association) and Polymerization

Approaching now the quantitative treatment of the polymerization in terms of statistical mechanics, it may be noted that one of the most lucid presentations of the subject is furnished by the recent work of Frenkel[309] at the Leningrad Physico-Technical Institute.

It was shown that the theory of the process of condensation, as developed by the above author, may be applied, with the negligible modifications, to the process of polymerization, i.e., to the formation of long-chain molecules built up by the union of separate links of the monomeric substance with one another. By the term " condensation " in this case is meant the formation of a liquid or solid body, but not that of the chemical condensation, which is taking place, for instance, in the producing of peptide chains (with the release of water) and equivalent in its results to the usual polymerization. The distinction of the polymerization from that of the association, as designated above (e.g., the association of the water molecules in vapour, both the saturated and unsaturated, etc.), consists, first, in that it is effected on account of the valence (chemical) bonds, and not through van der Waal's forces. It should be remarked, however, that in many instances (of such substances as carbon, metals, salts) the forces binding the particles in the solid or liquid state are also the " chemical " forces and not those of van der Waal, but with the implicitly expressed saturation, i.e., with the saturation not impeding the formation of the " condensate " of any great magnitude, and, secondly, in that the combining of the particles with one another is realized not in the three dimensions, but in one direction only. Due to this circum-

stance, the peculiarity of the chemical forces, expressed in the saturation effect, is not manifest during the polymerization, so that the latter, just as that of the condensation, can be continued, in principle, ad infinitum.

A long molecular chain formed during the polymerization thus represents the monodimensional analogue of a crystal, whereas the initial monomeric substance is an analogue of vapour (if it is in the dissolved condition), or that of a liquid (in the pure state). This analogy is broken only by the fact that the energy of the free ends of the molecular chain, playing the role of the surface energy of crystal, does not depend on the magnitude (i.e., the length) of the latter.

Polymerization and Crystal-formation Analogy

This circumstance precludes the possibility of the phenomena of super-saturation (or super-cooling) in the course of polymerization. In all other respects the statistical theory of polymerization differs from the statistical theory of condensation merely by quantitative details.

From the standpoint of the thermodynamic equilibrium, during the transit of vapour or liquid into the crystalline phase, it should result in the formation of a monocrystal. In precisely the same fashion, from the angle of the statistical mechanics, the polymerization should have led, at first glance, to the formation of a single giant polymeric molecule, whose length is limited only by the initial quantity of the monomer. The fact that in the actual polymerization there is formed not one macromolecule, but a great number of the macromolecules of various lengths, could have been explained, at first sight, by analogy with the formation during crystallization of a polycrystalline aggregate in place of a monocrystal, i.e., not from the angle of statistics, but from that of the kinetics of the process. As is known, however, the kinetics of the crystallization process is, mainly, determined by the conditions of the formation of the nuclei of the crystalline phase, i.e., connected with the phenomena of the super-cooling, which, as it was just stated, cannot occur in the case of the polymerization processes.

Another reason for the fact that during the polymerization there takes place the aggregation of the macromolecules of different lengths, instead of a single "monomacromolecule," corresponding to the monocrystal, it attributable, most probably, to the circumstance that van der Waal's forces of the interaction between the macromolecules are very feeble in comparison with the chemical forces uniting their links with one another, while in the event of the crystallization the forces of the interaction between the crystals (on their touching one another) have the same character and order of magnitude as the forces of the interaction between the atoms in a discrete crystal. Thus, if in the case of the crystallization it is necessary to introduce the coefficients of activity into the formulas for the chemical equilibria of aggregates of the various sizes, then, in the event of the polymerization the value of these coefficients may practically be considered as equal to unity.

Polymerization in Polypeptides

In many cases the formation of long filamentary molecules is accompanied by the liberation of the small atomic groups. Thus, for example, the emergence of the peptide chains from the amino acids is conditioned by the release of one water molecule for each peptide bond. This process, in contradistinction to the usual polymerization, is designated as the "condensation" (the "chemical" as distinct from the "physical" condensation as defined before).

The statistical theory of the polymerization, whose main outline will follow in due course, may be readily applied also in the case of such a "chemical" condensation, although the kinetics of both processes in several respects is substantially different. None the less, in the statistical treatment of these phenomena the primary significance attaches to the

presence of a substance released during the "condensation" and expended in the splitting off of the molecule into the smaller units, as, for example, that of water in the splitting of the peptide molecules into amino acids of low molecular weight.

Deductions

From the analytical considerations, as presented above, the fundamental problems of the polymerization may be summarized as follow:—

A.—The clarification of the mechanism and kinetics of the polymerization reaction. As a means to accomplish this, it will be necessary to select the simplest objects for the purpose, and to ascertain the applicability of the chain theory to the polymerization reaction for both in the gaseous and the liquid phases. It will be required also to elucidate the dependence of the process on the form of the vessel (the validity of Semenoff's equation: $w_1 : w_2 = Z_1 : Z_2^2$), as well as the part played by the inert admixtures, the positive and negative catalysts of the polymerization. Doubtless a great role here will be played by the Raman effect. Further, of special importance should be considered the group of the experimental works with the view to bringing to light the nature of the active centres, in the first place with the help of the mass-spectrograph, determination of the excitation potentials, the ionization of the ends of macromolecules.

B.—The next wide group of works comprises the structural problems: the length and the configuration of the molecules. The character of the physical and chemical bridges as inner bonds in the macromolecule, the degrees of freedom of the parts of the macromolecule and of itself in all its entirety. The X-ray and electron optics appear to be in this field the most direct methods at present available.

C.—The catalytic polymerization, activated by the application of one type of reagents (positive catalysts, accelerators), or de-activated, stabilized and arrested by the introduction of another type of substances (negative catalysers, decelerators, inhibitors).

D.—The study of an obscure question concerning the nature of the chemical strength properties of polymers, and the development of the optimum conditions of the technological regime for the synthesis of new polymeric products with desired characteristics.

Above all, it should be remembered that the reaction of polymerization is a typically "border-line" problem of chemical physics, the comprehensive approach to which and the wide co-operation of physicists, are urged by the very essence of the problem.

(To be continued)

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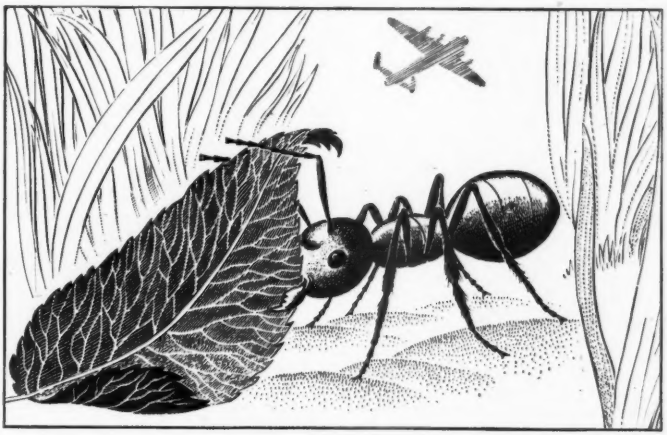

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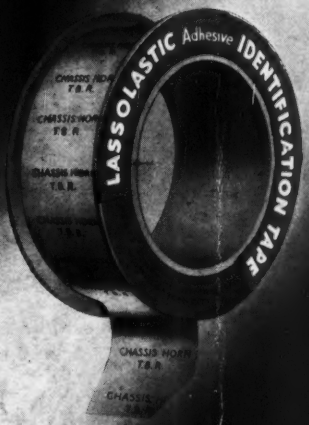

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